U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-259 861

An Improved Method for Determining Organics in Water by Activated Carbon Adsorption and Solvent Extraction

National Environmental Research Center, Cincinnati, Ohio

Jul 72

322079

PRE-PUBLICATION COPY

PB 259 861

[illegible]

Nr 15 [illegible] NTIS

[illegible]

AN IMPROVED METHOD FOR DETERMINING ORGANICS IN WATER BY ACTIVATED CARBON ADSORPTION AND SOLVENT EXTRACTION

by

Ralph W. Buelow, J. Keith Carswell and James M. Symons

Water Supply Research Laboratory
National Environmental Research Center
U.S. Environmental Protection Agency
Cincinnati, Ohio

July, 1972

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

BIBLIOGRAPHIC DATA SHEET

1. Report No.

2.

3. Recipient's Accession No. PB-259 861

4. Title and Subtitle
An Improved Method for Determining Organics in Water
by Activated Carbon Adsorption and Solvent Extraction

5. Report Date Jul 72

6.

7. Author(s)
Ralph W. Buelow, J. Keith Carswell, and James M. Symons

8. Performing Organization Rept. No.

9. Performing Organization Name and Address
National Environmental Research Center
Cincinnati, Ohio
Water Supply Research Lab.

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Organization Name and Address

13. Type of Report & Period Covered

14.

15. Supplementary Notes
(PC A06/MF A01)

16. Abstracts

In the past, the expense and inconvenience of the available methods for measuring the general organic content of water using activated carbon adsorption and solvent extraction prevented many water treatment plant operators from measuring this important parameter in their finished water. The purpose of this investigation was to provide the waterworks industry with a convenient, reliable procedure for measuring organics in water by this technique. Field testing of the procedure has demonstrated that it meets the basic objectives originally set forth and should be attractive to water plant operators. Sampling various types of waters showed that this technique can determine extract concentrations within about a ten-fold range in organic content between clean water and surface water heavily influenced by upstream discharges of wastes. this paper describes in detail the variables investigated during the development of this method.

17. Key Words and Document Analysis. 17a. Descriptors

*Activated carbon,
*Water analysis,
*Organic compounds,
*Measuring instruments,

Water pollution,
Sampling,
Absorbers(materials),
Field testing,
Monitoring,

Concentration(composition),
Drinking water
Toxicity,
Gravimetric analysis,
Design criteria,

Performance evaluation

17b. Identifiers/Open-Ended Terms
*Water pollution detection.

17c. COSATI Field/Group 13 B 14 B

18. Availability Statement
National Technical Information Service
Springfield, Virginia 22161

19. Security Class (This Report) UNCLASSIFIED

20. Security Class (This Page) UNCLASSIFIED

21. No. of Pages 117p

22. Price 5.50/3.00

PRE-PUBLICATION COPY

AN IMPROVED METHOD FOR DETERMINING ORGANICS IN WATER BY ACTIVATED CARBON ADSORPTION AND SOLVENT EXTRACTION

by

Ralph W. Buelow, J. Keith Carswell and James M. Symons

Water Supply Research Laboratory
National Environmental Research Center
U.S. Environmental Protection Agency
Cincinnati, Ohio

July, 1972

TABLE OF CONTENTS

Page

Introduction 1

Background 2

  High-Flow Carbon Adsorption Method Sampler 3

  Low-Flow Carbon Adsorption Method Sampler 4

  Current Studies 5

Sampler 8

  General Concept 8

  Sample Column Size 8

  Type of Activated Carbon 9

  Operational Variables 11

    Volume of Sample (Length of Exposure) 11

    Contact Time (Sample Flow Rate) 16

    Types of Waters to be Sampled 17

  Simplification of Design and Operation 20

    Design 20

    Operation 20

      Sampling 20

      Flushing 25

    Fabrication 25

    Handling of Sample Column 26

    Handling the Sampler 27

  Field Experience 27

Handling the Exposed Activated Carbon 31

  Removing the Activated Carbon from Column 31

  Drying 31

Page
    Drying Temperature 32
    Minimum Drying Time 33
  Maximum Length of Drying 35
    Mechnical Convection Ovens 35
    Gravity Convection Ovens 36
  Storage of Dried Activated Carbon 37
Extraction 39
  General Concept 39
  Influence of Number of Extraction Cycles 40
    General Operation 40
    Operating Limit 42
  Variation and Control of Cycle Times 47
  Extract Drying and Weighing 49
  Determination of Blank Values 55
  Extraction Solvent Reuse 58
  Equipment Cost and Size Reduction 59
    Cost 59
    Size 60
  Typical Extraction Schedule and Time Requirements 60
  Reproducibility 64
Discussion 67
  General Improvements 67
  Reproducibility 68
  Field Data 70a
    Increased Yield 70a
    CCE-m and CAE-m Concentrations 70a

Page

Conclusions 74

Acknowledgements 75

Glossary 77

References 79

Appendix 82

AN IMPROVED METHOD FOR DETERMINING ORGANICS IN WATER BY ACTIVATED CARBON ADSORPTION AND SOLVENT EXTRACTION

by

Ralph W. Buelow, J. Keith Carswell and James M. Symons
Respectively, Research Engineers, and Chief, Standards Attainment Br., Water Supply Research Laboratory, National Environmental Research Center, Office of Research and Monitoring, U.S. EPA.

In the past, the expense and inconvenience of the available methods for measuring the general organic content of water using activated carbon adsorption and solvent extraction prevented many water treatment plant operators from measuring this important parameter in their finished water. The purpose of this investigation was to provide the waterworks industry with a convenient, reliable procedure for measuring organics in water by this technique.

cont on
pg 2

This was accomplished by developing a small, reliable, simple-to-operate sampler that passes about 60 liters of water (2 day sampling period) through 70.0 grams of granular coal-based activated carbon at a sampling rate of 20 ml/minute (4.5 minute contact time). The miniaturization of sampling equipment and the resultant reduction in equipment size for sample drying and extraction reduces the cost over previous carbon adsorption methods. The sample volume was chosen as a compromise and is satisfactory for most waters. As a companion to the sampler, a small extraction apparatus is used to extract the dried activated carbon with about 450 cycles of chloroform followed by about 450 cycles of 95% ethyl alcohol. Although the elapsed time for sampling is 2 days; adsorbant drying, 1 day, solvent extraction, 5 days, and extract drying 2-3 days, the number of actual man-hours required for the determination is less than 6. The determination is called Organics-Carbon Adsorbable (O-CA).

Submitted for publication in the Journal of the American Water Works Association.

con't from pg 1

Field testing of the procedure has demonstrated that it meets the basic objectives originally set forth and should be attractive to water plant operators. Sampling various types of waters showed that this technique can determine extract concentrations within about a ten-fold range in organic content between clean water and surface water heavily influenced by upstream discharges of wastes. This paper describes in detail the variables investigated during the development of this method.

BACKGROUND

The possibility of the presence of taste and odor producing and/or toxic organic chemicals in drinking water is of concern to all connected with the provision of safe, esthetically pleasing water to the American consumer. If the quality of drinking water is to be protected, monitoring of organics should be part of any quality control program. Difficulties arise, however, as monitoring for most specific organics is beyond the capabilities of most water suppliers at this time (1972). This problem can be overcome somewhat, however, by monitoring for the general organic content of water and assuming, as is done with the coliform test, that if this material is below a certain concentration, the chances of problems from odorous or toxic material are reduced.

Each of the methods currently (1972) available for organic analysis have some disadvantages for use in water treatment plants, e.g., expense of equipment, complexity of analysis, and/or incompleteness of yield. While total organic carbon (TOC) analysis uses an unconcentrated sample, the equipment is expensive. Typical concentrating techniques are liquid-liquid extraction, freezing, vacuum rotary evaporation, reverse osmosis, and adsorption on resin or activated carbon. Of these, in spite of some limitations, the activated carbon adsorption method was chosen for this study because of its simplicity and its history of use in water supply and pollution control practice, dating back to 1952 (1,2,3,). After desorption from the activated carbon, the organics can be quantified gravimetrically or analyzed by gas chromotography, infra-red spectroscopy, or mass spectroscopy. Because of simplicity, the gravimetric method was chosen in this study.

High-Flow Carbon Adsorption Method Sampler

The sampler developed in 1951-52 sampled 5,000 gallons of water which passed through it at a 0.25 gpm (945 ml/min) flow rate. In subsequent years, this sampler was named the "High-Flow Carbon Adsorption Method (CAM) Sampler," (See Glossary, p. 77). The details of construction and operation of this type of sampler for finished water and of the procedure for the extraction of the activated carbon with chloroform to recover the adsorbed organics, carbon-chloroform extract (CCE-hf), was published in February 1962 (4).

The procedure was adopted as a "tentative" standard method effective March 1, 1962. (Note: Because the concentration of CCE may vary depending on the method of collection and extraction, additional lower case letters are proposed to identify the method used to obtain the data.) An alternate to the original sampling device was proposed by Taylor, Smith and Coene in 1964 (5). This method was subsequently included in the 12th Edition of Standard Methods for the Examination of Water and Wastewater.

Although the sampler had operational difficulties and was somewhat inefficient in adsorption and the extraction procedure was cumbersome, troublesome to perform, and less than completely efficient in desorption, the method for the first time did permit an evaluation of the organic content of many previously unsampled waters. Ettinger analyzed CCE-hf data from many locations in 1960 (6) and found that 97 percent of the concentrations were equal to or less than 200 µg/l. He also pointed out that chlorinated pesticides, nitriles, a substituted nitrobenzene and aromatic ethers, among other organics, had been recovered from the extract. Later, Heuper and Payne (7) showed the carcinogenic properties of CCE-hf material. Therefore, in spite of its difficulties, determination of organics in water by this technique was helpful to the water supply industry. In recognition of the usefulness of monitoring organics ,the revised U.S. Public Health Service Drinking Water Standards, published in the Federal Register (8) March 6, 1962, included a CCE-hf limit of 0.2 mg/l.

Low-Flow Carbon Adsorption Method Sampler

The high-flow CAM method did need improvement, however, and the first important changes were published by Booth et al. in 1965 (9). Additional information is contained in References 10, 11 and 12. The referenced researchers showed that more organic matter could be adsorbed on the activated carbon if the sample was passed through the sampler more slowly. This led to the development of the "Low-Flow CAM Sampler," which employs a sample flow rate of 120 ml/min (5.3 min. contact time) instead of 945 ml/min (0.25 gpm - 0.6 min. contact time), a sampling period of one week instead of two, and could be used on raw as well as finished waters. In addition, this sampler used all "fine" carbon for adsorption and contained an improved method for measuring the total volume passing through the sampler. (10). This sampler is now (1972) commercially available. The 13th Edition of Standard Methods (13) included the Low-Flow Method as a companion to the High-Flow Method for the determination of general organics in raw water. With one exception, the extraction portion of the Low-Flow Method procedure is the same as the High-Flow Method: A second extraction, with 95 percent ethyl alcohol as the solvent, is included in the Low-Flow Method. This extract is called CAE-1f. This measurement is important because of the work of Heuper and Payne (7) whose data were reanalyzed by McCabe (14) to show life-shortening in rats fed CAE material and the work of Rosen, Middleton and Taylor (15) who demonstrated that at least one synthetic organic, alkyl benzene sulfonate (ABS), was in the CAE rather than the CCE.

Current Studies

In spite of the improved adsorption of the low-flow rate

CAM sampler, with a corresponding increase in CCE and CAE concentrations, see Table 1 and Reference 11, the Low-Flow method has the following disadvantages; 1) the sampler is cumbersome and has some operational difficulties; 2) the exposed columns are heavy and awkward to package for shipping to the analyst, if this is required; 3) a large drying oven is needed; 4) the extraction equipment is large and expensive, requires special hoods, and does not provide for very vigorous extraction; and 5) finally, as pointed out by Allen, Pahl and Mayhan (16) the extraction procedures (13) are very vague and/or ambiguous in many details. Further, the Drinking Water Standards were not changed to correspond to this new measurement technique, so its use has mainly been confined to raw water.

The purpose of the project reported in this paper, an extension of the work started by Robeck and Dostal in 1962 (17) was to preserve the improvements made in the past, while incorporating changes:

1) to further improve the sampler by simplification, miniaturization, and enhancement of adsorption efficiency,

2) to make the extraction more convenient by simplification and miniaturization, and more vigorous by increasing the number of total cycles of solvent during the extraction period.

The resulting analytic determination, called Organics - Carbon Adsorbable (O-CA), is simpler and more reliable than previous techniques and therefore, water treatment plant laboratories and mobile laboratories, as well as large central laboratories should be able to perform the test. Further, the

TABLE 1

INCREASED ADSORPTION OF LOW-FLOW CAM SAMPLER COMPARED TO HIGH-FLOW CAM SAMPLER (DATA COLLECTED IN FOUR CITIES)

CCE			CAE		
High Flow mg/l	Low Flow mg/l	Ratio(LF/HF)	High Flow mg/l	Low Flow mg/l	Ratio(LF/HF)
<0.05	<0.05	-	<0.05	0.2	-
<0.05	0.1	-	0.1	1.2	12
<0.05	0.1	-	0.1	1.0	10
<0.05	0.1	-	0.1	1.1	11
0.1	0.2	2.0	0.1	1.2	12
0.1	0.1	1.0	0.1	1.1	11
0.1	0.3	3.0	0.2	1.2	6.0
0.1	0.2	2.0	0.2	1.0	5.0
0.1	0.4	4.0	0.3	1.1	3.7
0.1	0.2	2.0	0.3	1.4	4.6
0.1	0.3	3.0	0.3	1.5	5.0
0.1	0.3	3.0	0.3	1.6	5.3
0.1	0.4	4.0	0.3	1.5	5.0
0.2	0.2	1.0	0.3	1.2	4.0
0.2	0.4	2.0	0.3	1.2	4.0
0.2	0.3	1.5	0.3	1.2	4.0
0.2	0.3	1.5			
0.2	0.3	1.5			
	Mean	2.3*		Mean	6.8*
	σ	1.0		σ	3.3
	Range	3.0		Range	8.0
Relative Standard Deviation		43%	Relative Standard Deviation		49%

*Although the data are somewhat scattered, an increase in adsorption efficiency of the Low-Flow CAM Sampler is evident.

improved adsorption during sampling and improved recovery during extraction results in a better measure of the original organic content of the water. (Note, the proposed 1972 U.S. Environmental Protection Agency Drinking Water Standards contain a standard for O-CA based on the use of this improved measurement technique. The method cited in the Appendix has been proposed for inclusion in the next edition of Standard Methods.)

SAMPLER

General Concept

The large CAM sample column being used in the high- and low-flow rate CAM samplers contains such a large quantity of activated carbon that special glassware and hoods are required for extraction. Development of the miniaturized CAM sampler (Mini-Sampler) described herein was a result of the desire to eliminate the need for expensive, large-size, special extraction equipment by reducing the quantity of activated carbon in the CAM sampler, while maintaining the improvement in contact time and volume measurement developed by Booth and coworkers (9,10,11,12). Further, the work aimed at simplifying the sampler to eliminate some of the operational difficulties experienced with the current (1972) CAM samplers, to assure that the resulting equipment could be conveniently operated by water treatment plant operators. The authors hope that the availability of a reliable, simpler-to-operate, low-maintenance sampler will stimulate more water treatment plant operators to measure the general organic concentration in their water.

Sample Column Size

The quantity of adsorbant used in the Mini-Sampler was determined mainly by the capacity of the selected extraction apparatus. Robeck and Dostal (17) reported that about 70 grams of coal-based granular activated carbon could be extracted in a 55/50 Soxhlet extraction apparatus using a 43X123 mm cellulose extraction thimble and that use of this amount of adsorbant would provide a measurable quantity of extract. Therefore, an adsorbant quantity of 70.0 grams was chosen.

Several different sizes and shapes of polyvinyl chloride (PVC) columns to hold the 70.0 gms of activated carbon were tested. Extract quantities were not affected by changing column diameter and length as follows: column sizes of 1.5 in. I.D. x 6 in., 2 in. I.D. x 3.5 in. and 2 in. I.D. x 3 in. all produced similar results. To keep the column as short and compact as possible, a 2 in. I.D. x 3 in. PVC pipe nipple was chosen for the sample column. The size of the assembled sample column is shown in the photograph (Figure 1).

Type of Activated Carbon

Booth et al. (9) continued to use "fine" activated carbon, Nuchar C-190 manufactured by Westvaco,* New York, New York, in his development of the Low-Flow CAM sampler. This activated carbon does not wet too easily and has a tendency to float, making it unacceptable for use in an upflow sampling column that does not restrict upward movement. Further, Robeck and Dostal (17)

---

*Mention of trade names or products does not constitute an endorsement by the Federal Government.

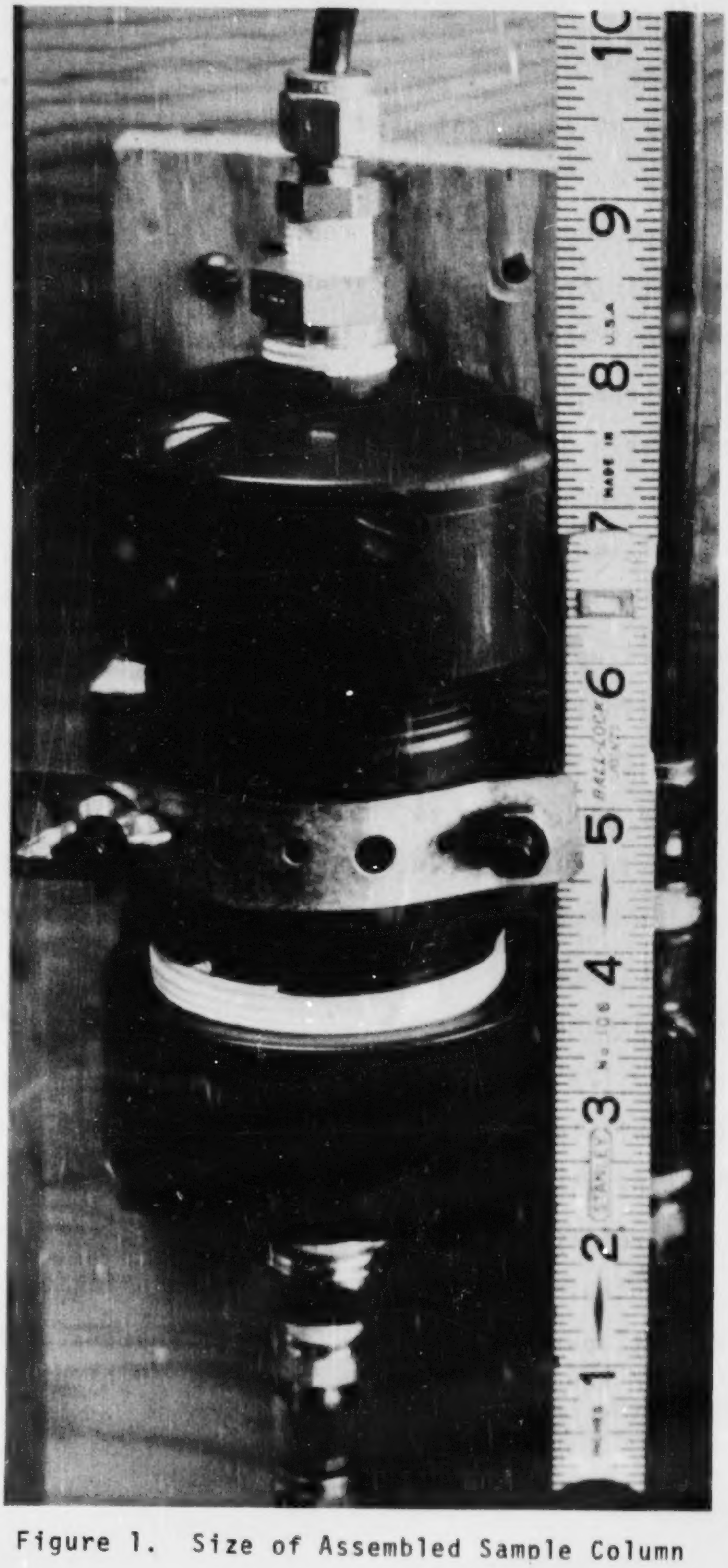

10
9
U.S.A.
8
MADE IN
7
6
5
4
3
STANLEY
2
1

Figure 1. Size of Assembled Sample Column

showed that coal-based granular activated carbon, GW, 10x30 manufactured by Pittsburgh Activated Carbon Co., now Calgon Corporation, was satisfactory for unconfined upflow sampling. Comparison of adsorption by the quantity of activated carbon that would fit in the extraction thimble showed an extract yield with GW, 10x30, about 1.3 times Nuchar C-190. For these reasons, the present (1972) equivalent of that activated carbon, Filtrasorb 200 (14 mesh x 40 mesh grain size) manufactured by the Calgon Corporation, Pittsburgh, Pa., was chosen as the adsorbant in this method.

Operational Variables

Volume of Sample (Length of Exposure)

Reid et al. (11) showed that the efficiency of activated carbon for adsorption of organics decreases as the quantity of adsorbed organics increases. Consequently, the smallest sample volume should be used that will provide a reasonable weight of extract, thereby maintaining high adsorption efficiency throughout the sampling period. Therefore, a study was made to determine the best sample volume for the O-CA test.

This study consisted of sampling a given batch of Cincinnati, Ohio tap water at a constant sampling flow rate for four different sampling periods (different sample volumes) and comparing the resulting extract concentrations. This was done twice, one in the autumn (Test 1) and once in the winter (Test 2) when the organic content of the water was higher. Figure 2 shows that in both tests the CCE-m* concentration was only slightly influenced by

---

*See Glossary for definition and Appendix for method of determination.

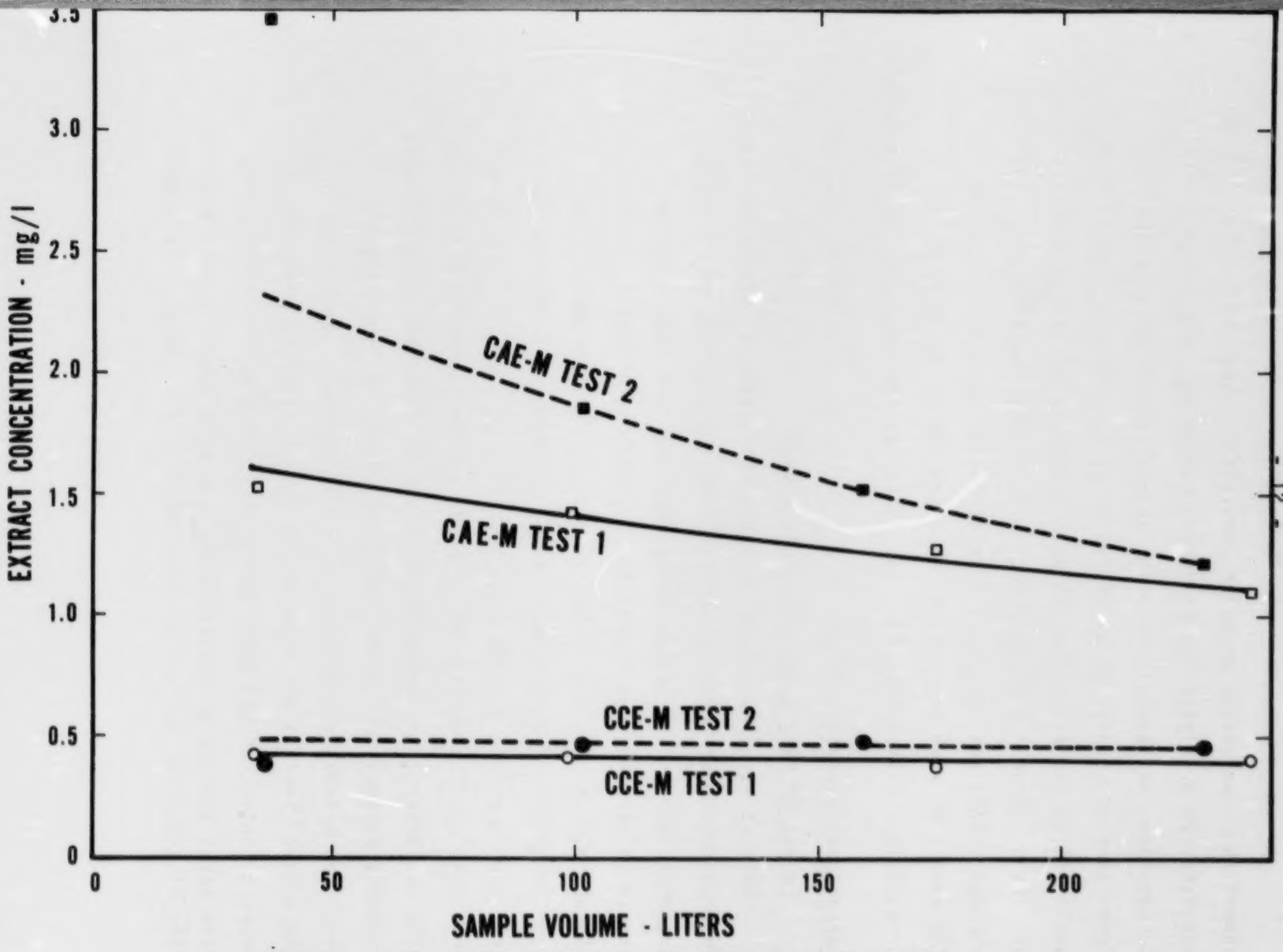


FIGURE 2 - INFLUENCE OF SAMPLE VOLUME ON CCE-M AND CAE-M

sample volume. A marked decline occurred in CAE-m* concentration as sample volume increased, however, and the higher organic content of Test 2 further increased the rate of decline.

Three constraints influenced the final recommended choice of a sample volume. These were: 1) the sample volume should be small enough to avoid excessive loss in organic adsorption efficiency, 2) the sample volume should be large enough to provide a reasonable quantity of extract, and 3) the sampling period should be convenient for water plant operators and others.

To investigate the loss in organic adsorption efficiency, the data in Figure 2 were replotted as a straight line on semi-log paper and the curves extrapolated back to the "y" axis (zero sample volume) to determine the theoretical extract concentration (C_0) at 100 percent adsorption efficiency. The percent adsorption efficiency C/C_0 x 100, was then calculated for various sample volumes and plotted in Figure 3.

These data show that loss in adsorption efficiency with increasing sample volume is not too great with CCE-m, but is a problem with CAE-m, particularly as the CAE-m concentration increases. This would suggest that a rather small sample volume should be recommended.

---

*See Glossary for definition and Appendix for method of determination.

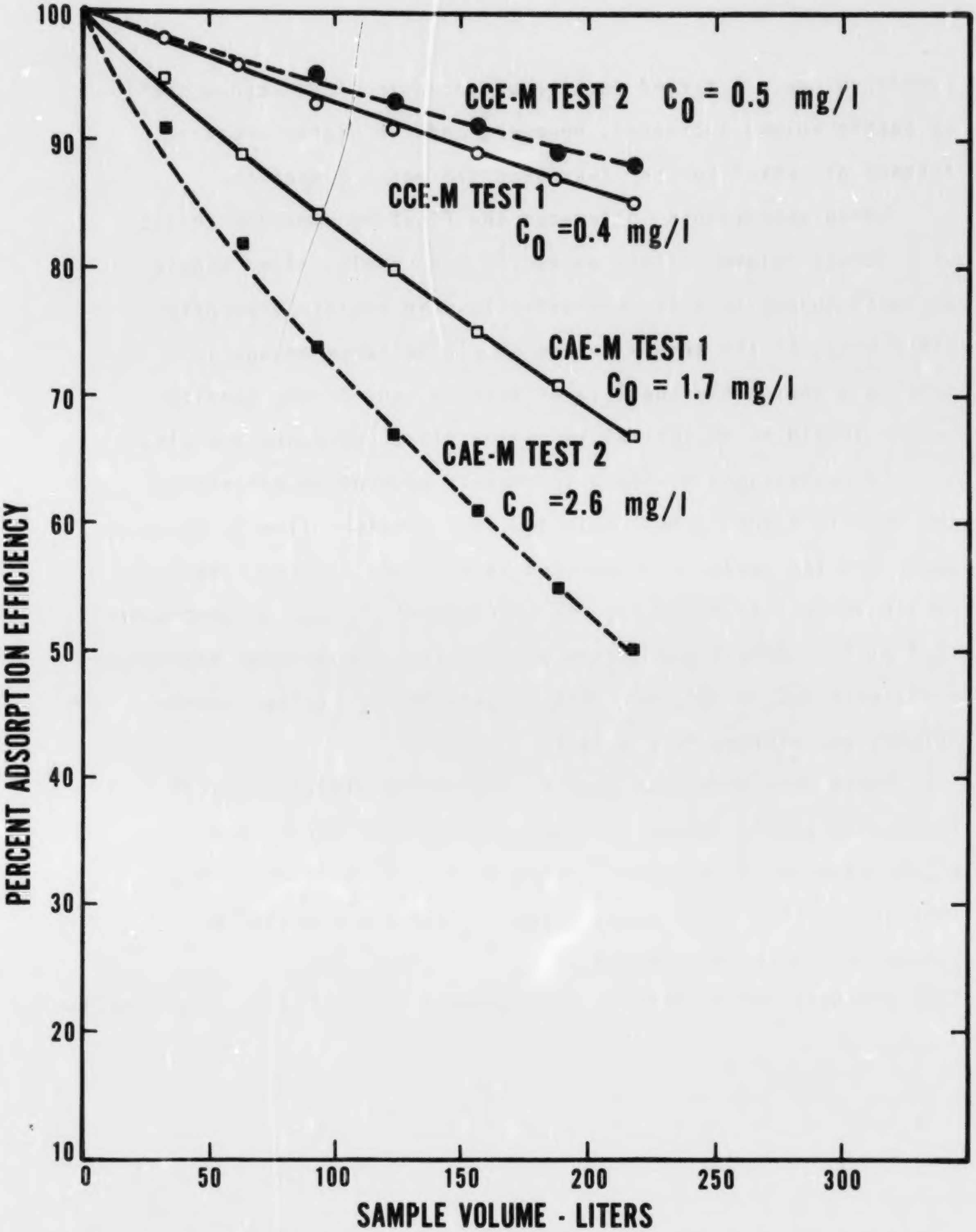


FIGURE 3 - INFLUENCE OF SAMPLE VOLUME ON ADSORPTION EFFICIENCY

Because the CCE-m concentration in a given water is much lower than the CAE-m concentration,as the sample volume decreases the quantity of CCE-m recovered becomes quite small. Further, as the sample volume decreases, sampling time also decreases (assuming a constant sample flow rate) and more samples must be collected each week if continuous monitoring is desired. This increases the extraction work load. As a compromise, therefore, a sample volume of about 60 liters was chosen. Using this sample volume and sampling waters containing organics at or near the proposed 1972 U.S. Environmental Protection Agency Drinking Water Standards (1972 DWS) concentrations, sufficient CCE-m will be collected while a satisfactory percentage of CAE-m will be recovered. About 1/18 of the adsorbant volume is used in the Mini-Sampler compared to the low-flow CAM sampler and about 1/20 of the total quantity of low-flow CAM sample volume is used in the new method, so the good adsorption showed by the low-flow CAM sampler is maintained.

The authors realize that at this sample volume, waters with an organic content well below the proposed 1972 DWS limits will produce small quantities of CCE-m and that recovery of CAE-m from waters with an organic content well above the proposed 1972 DWS will suffer. The sample volume was chosen to optimize reliability at or near the proposed 1972 DWS limits, however.

Contact Time (Sample Flow Rate)

Booth, et al. (9) studied the influence of the time the sample contacts the adsorbant on adsorption efficiency. They showed a great increase in organic yield from CAM samplers if the contact time was increased from 0.6 min (High-Flow CAM Sampler) to 5.3 min (Low-Flow CAM Sampler). Work by Robeck and Dostal (17) indicated that 20 ml/min was a satisfactory sample flow rate in their miniaturized CAM sampler. Therefore, the contact time resulting from this sample flow rate was investigated.

The theoretical contact time of water with the activated carbon in the Mini-Sampler at the flow rate of 20 ml/min was determined to be 3.9 minutes, based on the volume of the voids. A check under actual sample flow conditions with a sodium chloride tracer showed that the first passage of the salt solution through the activated carbon occurred in 3.3 minutes and the maximum salt concentration occurred at 4.7 minutes.

Because the contact time at the sample flow rate suggested by Robeck and Dostal (17) is somewhat shorter than in the Low-Flow CAM sampler, a study was made to determine whether or not lower or higher sample flow rates would influence organic yield. A given batch of Cincinnati, Ohio tap water was tested at sample flow rates of 10, 15, 20, 25 and 30 ml/minute. The corresponding contact times were 7.8, 5.2, 3.9, 3.1 and 2.6 minutes based on volume of the voids. The samplers were operated for different sampling periods so that each sampled about 65 liters of water.

The resultant data in Figure 4 show that over this range of contact times, CCE-m and CAE-m concentrations were unaffected. Therefore, the recommended sample flow rate is 20 ml/min and the recommended sample flow rate range is 18 to 22 ml/min, which is easily obtainable with the Mini-Sampler. As noted in the previous section, a total sample volume of about 60 liters is recommended. At these sample flow rates, a sampling period of 48 hours would yield a total sample volume of 62 liters (range 58 liters to 68 liters). Further, a 2-day sampling period allows "once-a-week" sampling without weekend work or nearly continuous sampling by collecting three samples per week, extracting them the following week.

Types of Waters to be Sampled

The Mini-Sampler was designed for sampling water containing organics mostly in the dissolved form. It was not designed to sample wastes. When the Mini-Sampler is used to sample finished water or low turbidity raw water, screening or pre-filtering devices, while not necessary, do serve as a safeguard against particles dislodged from supply lines blocking the valve openings. However, when turbid water is being sampled, e.g., settled water or raw surface water, an 80-mesh stainless steel screening device is needed in the upper constant head tank (Main tank) to prevent particulates from blocking the valves, see photograph (Figure 5). The particulates that pass through this screen do not interfere with the flow through the sampler. To date (1972) the Mini-Sampler has only been tested on moderately turbid raw surface water. The authors cannot judge at this time,

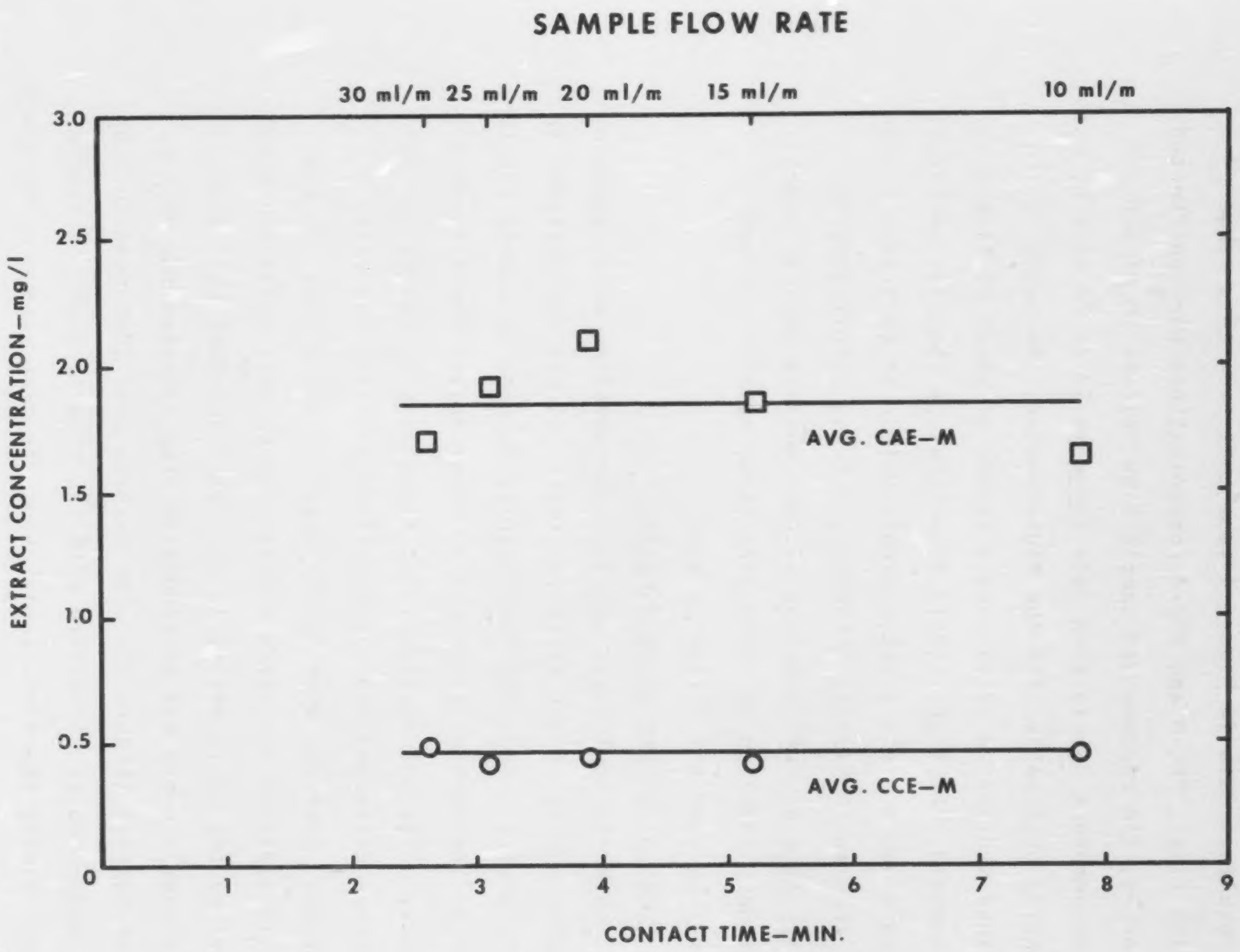


FIGURE 4
INFLUENCE OF CONTACT TIME ON CCE—m AND CAE—m

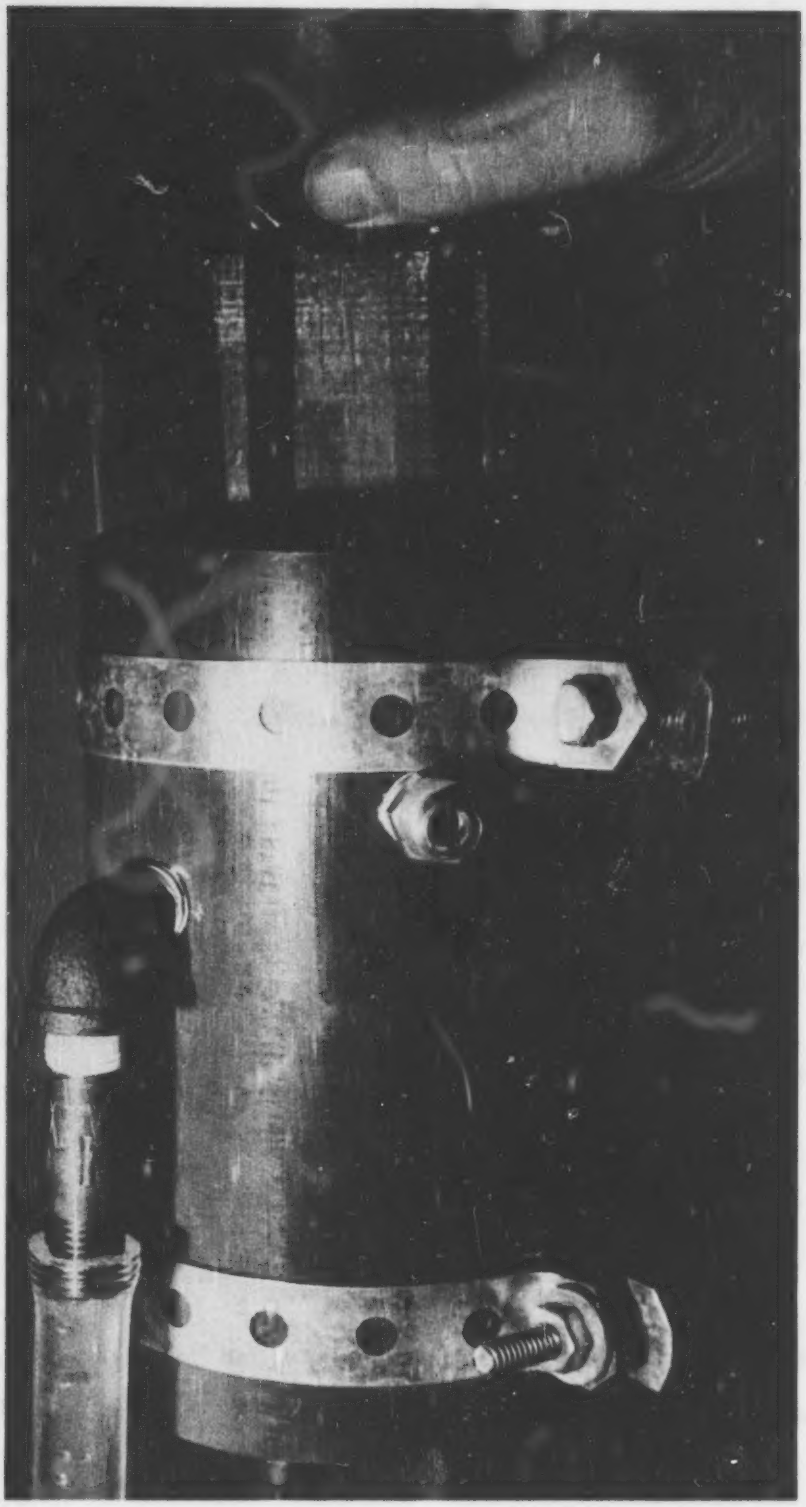


Figure 5 - Screening Device in Main Tank

therefore, whether or not it will sample extremely turbid surface water.

Simplification of Design and Operation

The Mini-Sampler was designed with the goal of keeping operation simple, reliable, and trouble-free. In order to accomplish this goal, a small, convenient, low-pressure, leakfree sampling device without pumps and float-control valves, that will operate reliably with a minimum of attention was necessary. Figure 6 is a photograph of the entire Model A of the Mini-Sampler, Figure 7 is a close-up of the sampling and volume-measuring boards, and Figure 8 is a schematic sketch. Figure 9 is a photograph of Model B, with a calibrated collection vessel, replacing the volume-measuring board.

Design

This sampler was designed to operate on line pressure although other methods of providing head can be used. It utilizes overflowing constant head tanks to provide gravity feed water supply to the sample column, thus eliminating the need for sample column feed pumps and level control float valves. Moving parts have been kept to the minimum and only consists of two solenoid valves, two electrical timers, a level controller relay, and a digital counter, all of which are very reliable and trouble-free.

Operation

Sampling

The Mini-Sampler is simple to operate and requires only one daily flow measurement after a sampling period has begun. Even this attention is not too critical because the sampler usually maintains

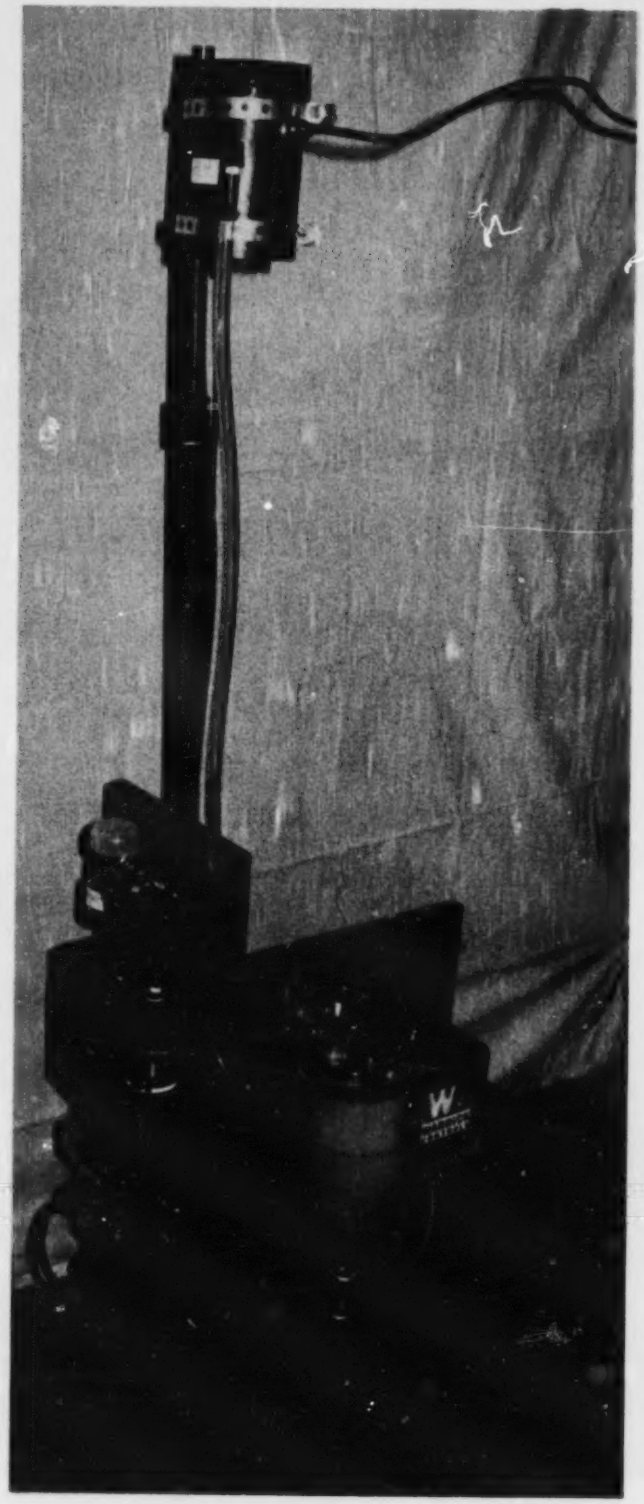


Figure 6 - Mini-Sampler-Model A
5-1/2 Feet High

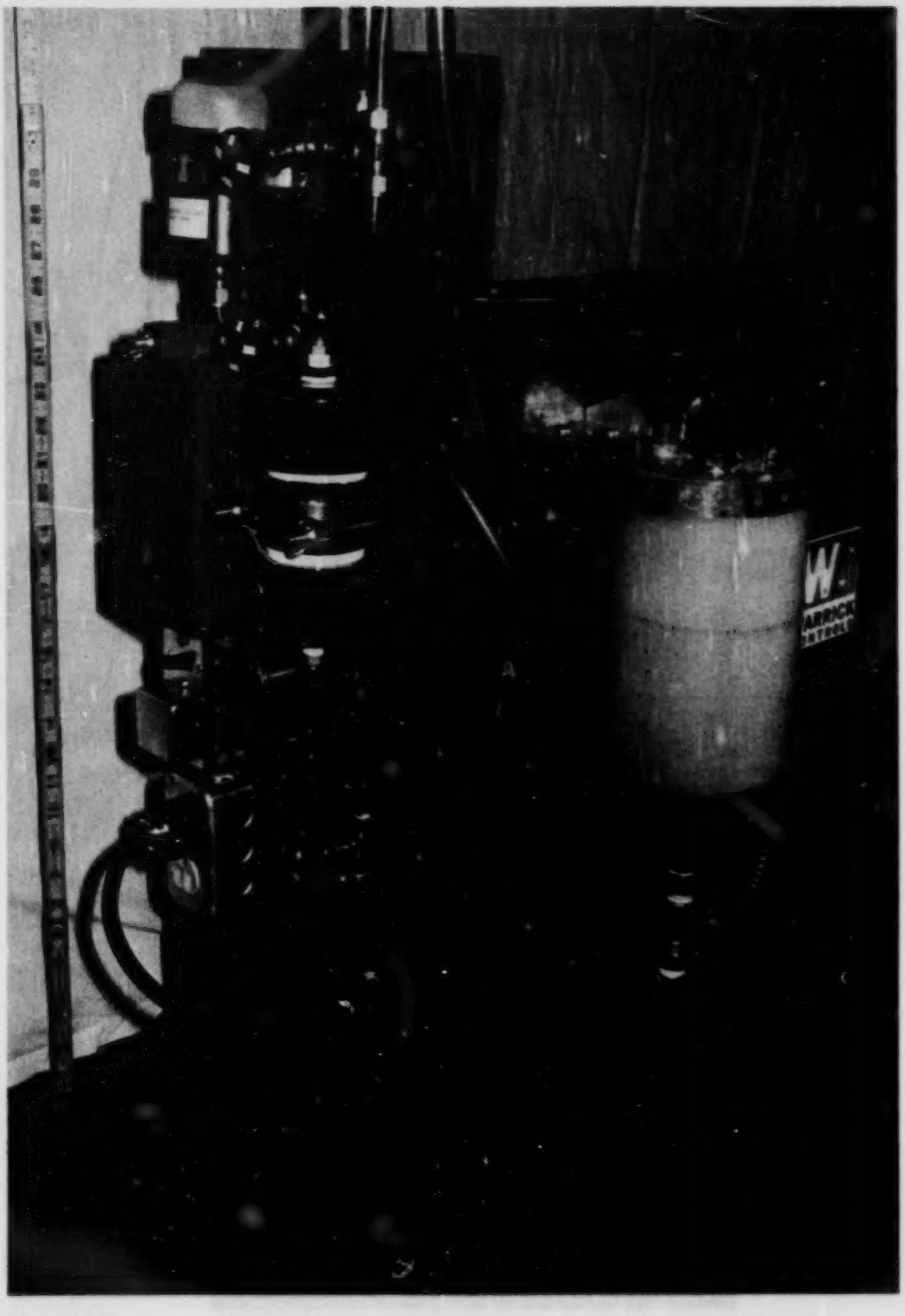

W
ARRICK
ONTROLS

Figure 7. Sampling Board (Left) and Volume Measuring Board (Right) in Assembled Position

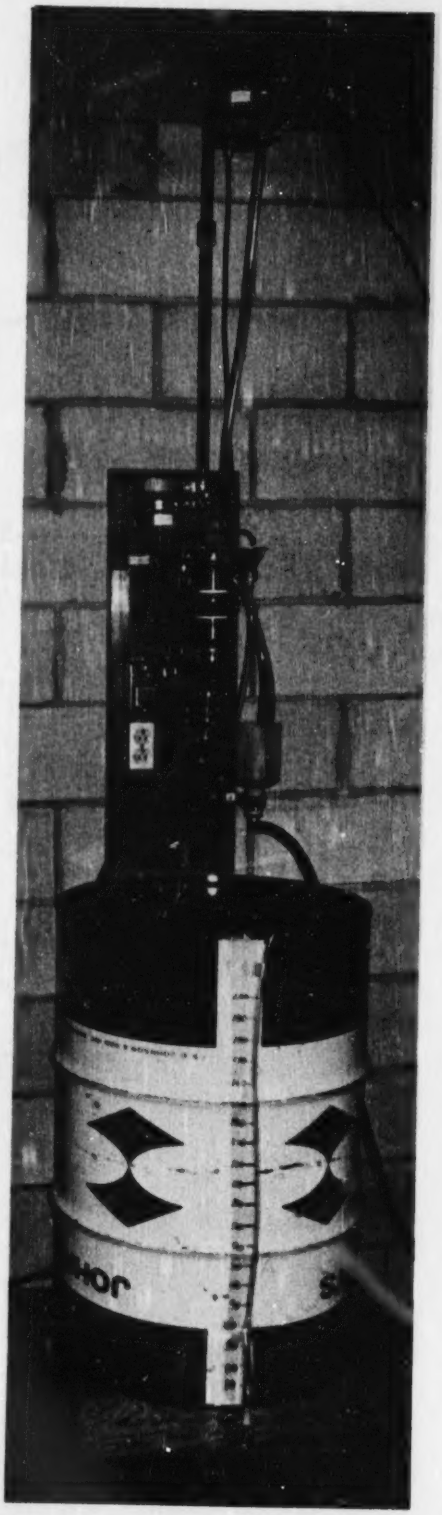
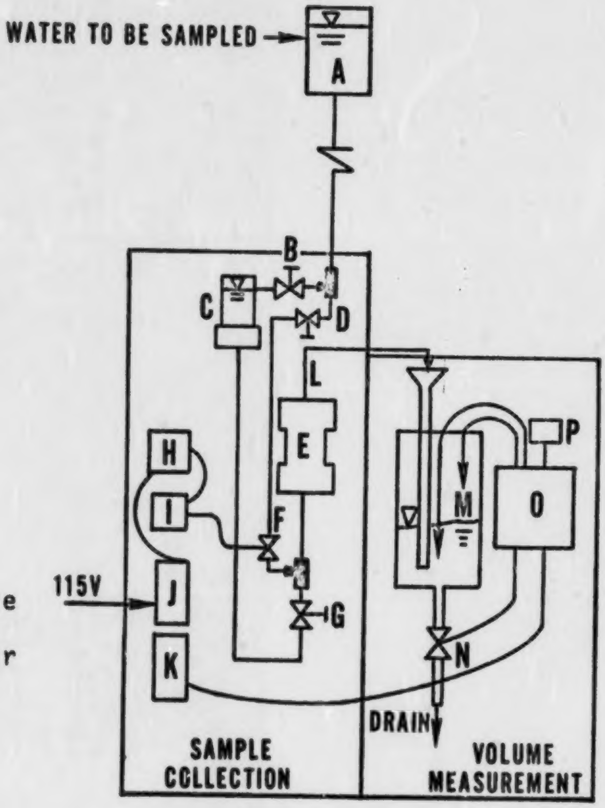


Figure 8 - Mini-Sampler - Model B With 55-Gallon Drum to Measure Sample Volume

FIGURE 8

SCHEMATIC OF MINIATURE CAM SAMPLER (MODEL A) (MODEL B DOES NOT HAVE PARTS M-P AND REPLACES THEM WITH A CALIBRATED COLLECTION VESSEL)

A - Constant Head Main Tank
B - Sample Column Feed Tank Valve
C - Sample Column Feed Tank
D - Flushing Valve
E - Sample Column
F - Flushing Solenoid Valve
G - Sample Column Flow Regulating Valve
H - 30-Minute Timer
I - Delay Timer - Set for 7-8 Seconds
J - Power ON-OFF switch
K - Duplex Outlet
L - Sample Column Outlet Tube
M - Volume Measuring Tank
N - Volume Measuring Solenoid Valve
O - Volume Measurement Control
P - Digital Counter Volume Recorder


WATER TO BE SAMPLED
A
B
C
D
L
E
H
I
F
G
115V
J
K
P
M
O
N
DRAIN
SAMPLE COLLECTION
VOLUME MEASUREMENT

nearly constant sampling flow. Within limits, a change in sample flow rate is not a problem, because total sample volume is measured using the system of Castelli and Booth (10). This system will provide a total sample volume regardless of flow rate. (Note: A second model, (B), of the Mini-Sampler can be used without the volume measuring apparatus, if the entire sample is discharged into a calibrated collection vessel after contacting the activated carbon.)

Flushing

The cornerstone of the reliable operation of the Mini-Sampler is the regular, periodic flushing of the activated carbon in the direction of sample flow. This operation, carried out automatically, prevents consolidation of the activated carbon during sampling, and/or an accumulation of air pockets that would impede the sample flow through the column. Therefore, to prevent column blockage, high-rate hydraulic flushing, (approximately 50 ml of sample during a 7-8 sec. interval, once every 30 minutes) has been provided to assure nearly constant sample flow rate. Flushing is accomplished with the same water that is being sampled, the head being provided by the 3 ft head tank and the flushing interval and duration being controlled automatically by timers.

Fabrication

While the authors hope the Mini-Sampler will eventually become comercially available, it can be fabricated by individuals. A parts list and construction details and a booklet entitled

"Determination of Organics - Carbon Adsorbable (O-CA) in Water" containing a detailed description of the Mini-Sampler is available from Director, Water Supply Research Laboratory, U.S. Environmental Protection Agency, 4676 Columbia Parkway, Cincinnati, Ohio 45268. No extensive machine shop work is involved in fabricating the sample units. Almost all parts are standard stock items. The exceptions are simple mounting brackets and straps that are made from wood, angle or strap metal. The cost of materials for Model A is slightly over $200 and for Model B, about $100, but a calibrated collection vessel must be provided with Model B. The Environmental Protection Agency had 15 Model A units built on contract by Sea World Research and Development Laboratory, North Wilbraham, Massachusetts 01067.

Handling of Sampling Column

The small size of the sampling column makes it very easy to handle. If necessary, the column can be easily shipped through the U.S. Postal Service in a 10 in. high by 3-1/4" I.D. mailing tube. Paper or other packing materials must be placed inside the ends of mailing tube to prevent lengthwise movement of the column. For repeated use of the mailing tube, its ends must be reinforced with filament tape.

Handling the Sampler

The authors have tried to design the Mini-Sampler to be useful both as a permanent installation at a given location for quality control, as well as a portable monitor, useful for surveillance. Model A is a 2-package arrangement, shown in the photograph (Figure 10). The carrying cases are made of wood, the sample collection package case dimensions are 32-1/2" X 10-1/2" X 8", and the weight, 30 pounds. The sample volume measuring package case dimensions are 27-1/4" X 12-1/2" X 8", and the weight, 23 pounds. The size of these packages allows them to be easily transported by automobile, as baggage on an aircraft, or by U.S. Postal Service. Model A is self-standing, using the sample volume measuring package case as the base, Figures 6 and 7. Model B is just one package which is the sample collection package described in Model A. Both models are easily assembled and disassembled.

Field Experience

To test the convenience of setting up the Mini-Sampler and its reliability of operation under actual field conditions, four Mini-Samplers were placed in three water treatment plants. At two plants finished water was monitored and at the third location both settled and finished water was sampled. The Mini-Samplers were operated for at least 11 weeks at each location. In addition, it has been used as a surveillance tool at 5 water treatment plants.

Field experience to date has been excellent. No hydraulic failures to stop the sample flow through the column have occurred. In one instance, the sample flow-rate slowed to 12 ml/min after one day of operation at a new installation. This was caused by

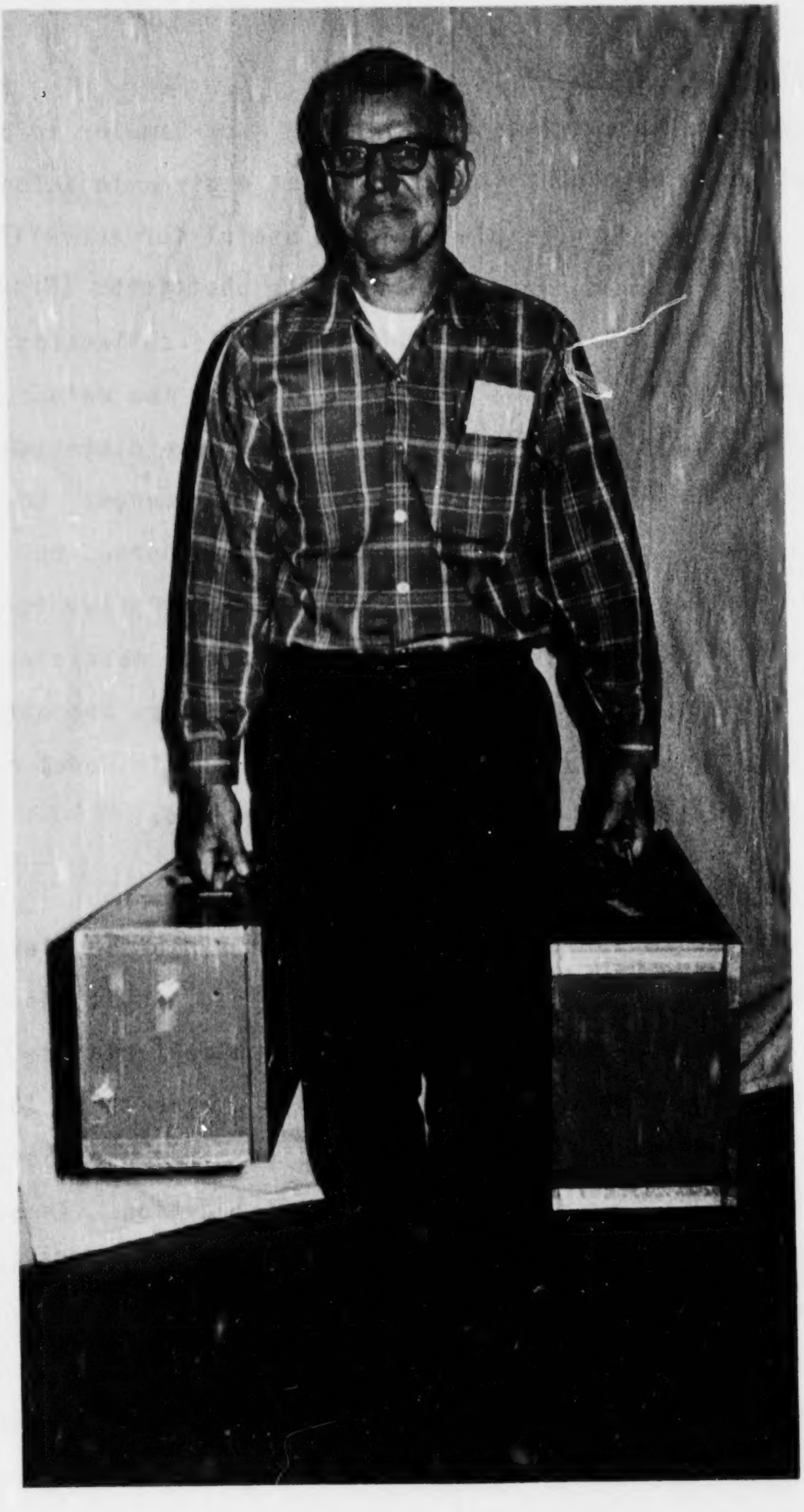


Figure 10 - Mini-Sampler - Model A - Packed for Transport

a defective flushing frequency regulating timer that was not properly activating the delay timer for the flushing cycle. Once this was corrected, no further problem with this unit occurred. This incident of serious sample flow-rate decrease was the only one experienced during the collection of 65 samples at 8 field locations.

During the first nine months of operating the Mini-Sampler, which included the field experience described above, the flushing cycle frequency was once every hour for 15 seconds at a 400 ml/min rate. This provided a flushing volume of approximately 100 ml. This testing period spanned April through December, 1971.

During January 1972 some unexpected fluctuations in sample flow rate occurred in one sampler being used in our laboratory. The sample flow rate would range from 22 to 16 ml/min. Although this was nearly within recommended operating limits for the sampler, it was not desirable. In the authors' judgment these fluctuations were caused by cold water conditions that aggravated air binding problems in the column.

Observation of the sample flow rate showed that it was constant for more than 30 minutes following flushing and decreased sharply during the last 15 minutes before flushing. To avoid this problem, the flushing frequency was changed to 30 minutes using the 400 ml/min flushing rate for 7-8 seconds and a flushing volume of 50-55 ml. This increased flushing frequency solved the sample flow rate fluctuations problem without increasing the total flushing volume during the sampling period. These two problems with sample flow rate change further emphasizes that flushing is the key to successful operation of the Mini-Sampler.

Three other important factors were confirmed during this field testing:

1. No difficulty was experienced in sampling settled water containing carry-over floc. Also, a Mini-Sampler was operated for several weeks on raw Ohio River water without clogging.

2. Although the instructions call for a daily check of the sample flow-rate, the experience in the field on finished and settled water was that if flushing was occurring properly, once the initial adjustment was made 1-2 hours after start-up, little or no sample flow-rate adjustment was needed during the sampling period. Therefore, in most cases, the Mini-Sampler will operate without adjustment during sampling, requiring only a daily check of operation. A daily check of the volume sampled also provides a record of the maintenance of the proper flow rate.

3. The field installations have demonstrated the ease of setting up the sampler quickly and without startup and leakage problems.

HANDLING THE EXPOSED ACTIVATED CARBON

Removing Activated Carbon from Column

The activated carbon can be easily removed from the column by removing one of the PVC end caps and tapping the two PVC sections together over a drying tray. The remaining activated carbon adhering to the column surfaces is then washed into the tray using a squeeze bottle and distilled water. The excess water is drained off by tipping the drying tray and screening the drainage to recover any activated carbon granules that might drain off.

Drying

Allen, Pahl, and Mayhan (16) pointed out the importance of drying exposed activated carbon properly. The activated carbon must be almost dry as excessive moisture interferes with the subsequent extraction. On the other hand, excessive heat can drive off volatile organics, thereby causing a negative error in the determination. The purpose of this phase of the study was to develop a procedure that would dry exposed activated carbon, quickly, gently, sufficiently and without the use of unusual equipment such as freeze driers. To satisfy the latter requirement only common drying devices were used. Three types were tested, two ovens and an incubator, as follows:

1. Blue M Mechanical Convection Oven, Temp. 38-260°C.
2. Despatch Gravity Convection Oven, 1100 Watt - Temp. to 205°C.
3. Thelco-Precision Gravity Convection Incubator, Temp. to 60°C.

In addition, for comparative purposes, some tests were made in a large mechanical convection oven used for drying the large CAM activated carbon samples.

To enhance drying, the exposed activated carbon sample is dried in a 8-7/8" X 5" x 2" stainless steel tray. The activated carbon depth, when spread evenly over the bottom of the tray, is approximately 3/16 in. This shallow depth allows for rapid and thorough drying throughout the sample.

Drying Temperature

To dry the activated carbon as gently as possible, a low drying temperature of 35°C was tried initially. The two drying ovens were difficult to regulate at this low temperature, however. If an incubator were used, it could be operated at this temperature. Many water treatment plants have incubators controlled to 35°C ± 0.5°C for the incubation of total coliform tubes or plates.

The difficulty in finding conventional drying ovens that could be regulated to 35°C prompted an investigation of whether or not a higher temperature for drying (40 ± 1°C) would result in a reduced extract weight because of volatilization. With difficulty, a mechanical convection oven was regulated at 35°C and two portions from a large batch of exposed activated carbon were dried for 48 hours. This was repeated with two more portions from the same batch, this time being dried at 39°C for 24 hours.

The extraction results shown in Table 2 indicate no significant difference in CCE-m and CAE-m concentrations recovered.

Table 2

EFFECT OF DRYING TEMPERATURE ON EXTRACTION RESULTS USING MECHANICAL CONVECTION DRYING OVENS

Sample	Drying Temp.°C	Drying Time,hr.	CCE-m mg/gm of Carbon	CAE-m mg/gm of Carbon
1	35	48	1.0	4.0
2	35	48	1.0	3.9
3	39	24	1.0	3.9
4	39	24	1.0	3.9

Minimum Drying Time

Table 3 shows that the 40°C mechanical convection ovens, Samples 1 and 2, dried the sample in 24 hours, while the 40°C gravity convection devices, Samples 3 and 4, dried them in 48 hours.

Table 3

EFFECT OF DRYING TIMES ON MOISTURE CONTENT*

Sample No.	Drying Apparatus Description	Temp. °C	Weight of carbon (grams) after drying 24 hr.	48 hr.	72 hr.
1	Dried in mechanical convection oven	40	70.7	70.7	70.7
2	Dried in large mechanical convection activated carbon drying oven	40	70.6	70.6	70.6
3	Dried in a gravity convection oven	40 (35-45)	74.7	70.6	70.6
4	Dried in a gravity convection incubator	40	76.1	70.5	70.5
5	Dried in mechanical convection oven	34	72.2	71.4	
6	Dried in mechanical convection oven	34	71.8	71.4	

---

*The activated carbon in these tests was first dried for 24 hours at 40°C in a mechanical convection oven, then 70.0 gm portions were soaked in distilled water for 24 hours prior to final drying.

Table 3 also shows that samples 5 and 6, dried at 34°C in a mechanical convection oven, did not dry satisfactorily, even in 48 hours. A drying temperature of 40°C was chosen because one of the aims in developing the drying procedure was to shorten the time required for analysis, and a 35°C drying temperature would extend the required drying time.

If a short drying time is not critical, however, an incubator controlled to 35°C ± 0.5°C for the total coliform test can be used for drying the activated carbon samples. The moisture driven off will not interfere with the total coliform test. Table 4 shows that under these conditions drying takes 2 days.

Table 4

EFFECT OF DRYING TIMES ON MOISTURE CONTENT*

Sample No.	Drying Apparatus	Temp. °C	Weight of Carbon (grams) after drying 24hr.	48 hr.	72 hr.
1.	Gravity Convection Incubator	35	73.5	69.9	69.9
2	Gravity Convection Incubator	35	77.0	70.0	70.0
3	Mechanical Convection Oven	40	70.0		
4.	Mechanical Convection Oven	40	69.9		

---

*For these samples 70.0 grams of stock activated carbon were soaked in distilled water for at least 24 hours prior to drying.

Note, the difference in the final "dry" weights in Tables 3 and 4 reflect a different experimental procedure. Originally, the stock activated carbon was predried at 40°C to remove any residual moisture prior to soaking and redrying in the test reported in Table 3. In the test reported in Table 4, this predrying was discontinued and the stock activated carbon was merely soaked and then dried.

The comparison of these results showed that nothing major is gained by pre-drying the activated carbon to test the drying capabilities of a drying device, should such a test be necessary. Therefore, the procedure to be used in determining the drying times required for any drying devices that are different from the recommended one is:Weigh out 70.0 gm portions of stock activated carbon, soak it in distilled water for at least 24 hours and then dry it until it returns to its original 70.0 gram weight or less, noting the time this requires.

Maximum Length of Drying

Mechanical Convection Ovens

Although 24 hours drying in a mechanical convection oven at 40°C ± 1°C is satisfactory, this procedure might be inconvenient if drying were started at the end of a working week. A study was conducted to determine if extended drying times would cause a loss in organics and result in reduced CCC-m and/or CAE-m concentrations. Four replicate exposed activated carbon samples were dried for various times and then extracted. The data in Table 5 shows that up to four days drying at these temperatures did not result in a measurable loss of extract.

Table 5

EFFECT OF DRYING TIMES ON RECOVERY OF CCE-m AND CAE-m

Test	Temp. °C	Drying Time (hr)	CCE-m mg/gm of Carbon	CAE-m mg/gm of Carbon
1	39	24	1.0	4.0
	39	48	1.0	4.0
	39	72	1.1	4.2
	39	96	1.1	4.1
2	40	24	0.9	3.6
	40	48	0.9	3.8
	40	72	0.9	3.5
	40	96	0.9	3.8

Therefore, drying the activated carbon for 24-72 hours in a mechanical convection drying oven at 40± 1°C, is recommended. (Note: when activated carbon is being dried, the oven should not be used for drying materials that would produce organic vapors as these would be adsorbed by the activated carbon.) This type of oven is much less expensive than the large drying ovens required for the high- and low-flow rate CAM sampler.

Gravity Convection Ovens

If a gravity convection oven or incubator is used, the drying time will have to be extended to a minimum of 48 hours. Table 6 illustrates that CCE-m and CAE-m values obtained from a split sample dried for 72 hours in 3 different types of gravity convection devices are comparable. The sample dried in the mechanical convection oven is included for comparison.

Table 6

COMPARISON OF MECHANICAL- AND GRAVITY-CONVECTION DRYING DEVICES

Type of Device	Temp. °C	Drying Time hr.	CCE-m mg/gm of Carbon	CCE-m mg/gm of Carbon
Mechanical Convection Oven	40	72	1.0	4.3
Gravity Convection Oven	40 (35-45)	72	1.0	4.3
Gravity Convection Oven	40 (35-45)	72	0.9	4.5
Gravity Convection Incubator	40	72	1.0	4.6

Storage of Dried Activated Carbon

Activated carbon samples should be dried as soon as they are removed from the sampler, or if shipped to a laboratory for extraction, as soon as they are received because of possible bacterial degradation of the adsorbed organics if the activated carbon remains wet. After they are dried they should be extracted promptly or stored under refrigeration (4°C) until they can be extracted. Screw-top wide-mouth pint glass jars make convenient storage containers. If the sample cannot be dried immediately, it should be refrigerated in the sample column until it can be dried.

To determine whether or not extended storage under the above prescribed conditions would cause any loss in organics, a large batch of exposed activated carbon was dried July 11, 1971 and put in storage. Six 70.0 gm portions of this material were extracted July 19, 1971 and two more 70.0 gm portions were extracted nearly two months later on September 13, 1971. Table 7 shows that no change in extract weights occurred during the extended storage.

TABLE 7

EFFECTS OF STORAGE OF DRIED ACTIVATED CARBON AT 4°C ON CCE-m AND CAE-m RECOVERY (DRIED ON 7/11/71)

Date	CCE-m mg/70 gm of Carbon	CAE-m mg/70 gm of Carbon
7/19/71	86.7	351.8
	88.0	354.2
	88.1	-
	86.4	-
	88.9	-
	84.2	-
9/13/71	88.7	364.2
	80.3	349.1

EXTRACTION

General Concept

Concurrently with the development of the Mini-Sampler, a series of investigations were conducted to develop an improved CCE-CAE extraction procedure using the extraction apparatus for which the new sampler was designed. Improvements sought over existing methods included:

1. A more vigorous extraction to remove more adsorbed material.
2. A less vague and/or ambiguous procedure emphasizing careful attention to detail.
3. A reduction in the size and the cost of the apparatus without a loss in the reproducibility of the analysis.
4. A reduction in the overall time required for the analysis.

As discussed below, all improvements except the latter were found to be possible. As with the Mini-Sampler, an extraction procedure was developed that is well within the capabilities of most water treatment plant laboratories and analysts, a primary goal of this study.

The basic extraction procedure described in this paper is an adaptation of the unpublished CCE procedure developed by Robeck and Dostal (17). Their method was devised to monitor the effectiveness of various water treatment processes in removing organic material from water, as measured by CCE concentrations.

The following is a brief, generalized description of the new extraction procedure. A detailed, annotated description of the proposed method appears in the Appendix. The basic steps of the new method are:

1. Extract organics from the dried activated carbon sample with chloroform in a 55/50 Soxhlet extractor for 44 hours at a cycle time of 6 min. ± 30 sec. per cycle.
2. Distill off excess extraction solvent to reduce its volume.
3. Transfer remaining solvent (containing the extract) to a tared vial.
4. Dry and weigh extract to determine CCE-m.
5. Dry activated carbon sample in extractor to remove chloroform.
6. Repeat extraction using 95 percent ethyl alcohol, a 48-hour extraction time, and a 6-1/2 min. ± 30 sec. cycle time.
7. Repeat remainder of the procedure to determine CAE-m.

Influence of Number of Extraction Cycles

General Operation

A Soxhlet extractor is designed to remove extractable materials from a sample by using a series of freshly redistilled volumes of some extraction solvent. The total volume of solvent siphoned through the sample is the sum of the individual volumes or cycles, and is thus directly related to the total number of cycles occurring within the extraction period.

In general, the greater the total volume of solvent (total number of cycles) used to extract a sample, the greater the total quantity of extractable material desorbed, although the relationship may not be linear. Therefore, the total number of extraction cycles to which a sample is to be subjected must be defined in some manner, if comparable results are to be obtained.

The current edition (1971) of Standard Methods (13) is rather vague on this point, noting only that "Extraction units [large] do not always siphon automatically." , "---regular siphoning is not necessary---", and "A voltage setting of 80 on the variable transformer is usually sufficient." Extractors that do not siphon establish an equilibrium-like flow-through condition in which the volume condensed (inflow) equals the volume discharged (outflow) back to the boiling flask. This condition subjects the activated carbon to an unknown number of extraction cycles. Comparison of data produced under these conditions is based on the assumption that similar transformer settings will produce a similar number of total extraction cycles in all instances. Because of the numerous variables that can influence the extraction process, the validity of this assumption is doubtful.

The 55/50 Soxhlet extractor used in the new extraction method does siphon regularly, at least over the range of cycle times investigated, and thus an operating limit based on the number of total extraction cycles is possible. Ideally, what is needed to control extraction is a simple, inexpensive device that counts extraction cycles without requiring modification of the extraction apparatus. Allen, Pahl and Mayhan (16) used a recording thermocouple placed between the boiling flask wall and a heating mantle, to measure the frequency and number of cycles in their extraction research. The cost of such a recording device was considered inconsistent with the goal of reducing the cost of the extraction apparatus, and the less expensive, though somewhat inconvenient method of stopwatch timing and calculation was selected to estimate the total number of extraction cycles. Until a practical counting device is developed, this is the method of choice.

Operating Limit

Robeck and Dostal's (17) original extraction procedure called for a CCE cycle time of about 4 min. per cycle. For the 24-hour extraction period they specified, this resulted in an activated carbon sample being subjected to about 360 total extraction cycles. With the 6-position, hot plate-type extraction heater used during most of the developmental stage of this method, a 4-min. cycle time was found difficult to attain with chloroform and impossible with 95% ethyl alcohol. This difficulty was attributed to a lack of sufficient heat transfer between the hot plate and the boiling flask and led to experimentation to determine what range of cycle times could be obtained within the capacity of the 6-position heater and what "total cycles" operating limit should be chosen.

Figure 11 shows typical CCE-m data obtained by the extraction of six replicate samples at various average cycle times for a 44-hour period. Similar data for CAE-m are shown in Figure 12. The replicate samples were obtained by exposing a large activated carbon sample to Cincinnati, Ohio, tap water. Following drying, the large sample was thoroughly mixed and divided into 70.0 g replicate portions for analysis.

As noted above, these Figures show that the gross weight of extract obtained increases with an increase in total extraction cycles, although in a non-linear manner. From these data, an operating target of about 450 total extraction cycles was chosen. This limit was chosen because; 1) after this number of extraction cycles the gain in extract weight per cycle is small, indicating the desorption under these conditions was essentially complete, and 2) a deviation from the limit of a few cycles caused by cycle time variations, see below, would not greatly influence the resulting extract weights.

A total elapsed time for the chloroform extraction was chosen as 44 hours to allow time for setting up on Monday morning and to have shut-down occur early on Wednesday morning. To operate within these two constraints, an average cycle time of 6 minutes per cycle was required. This value yields 440 total extraction cycles in 44 hours.

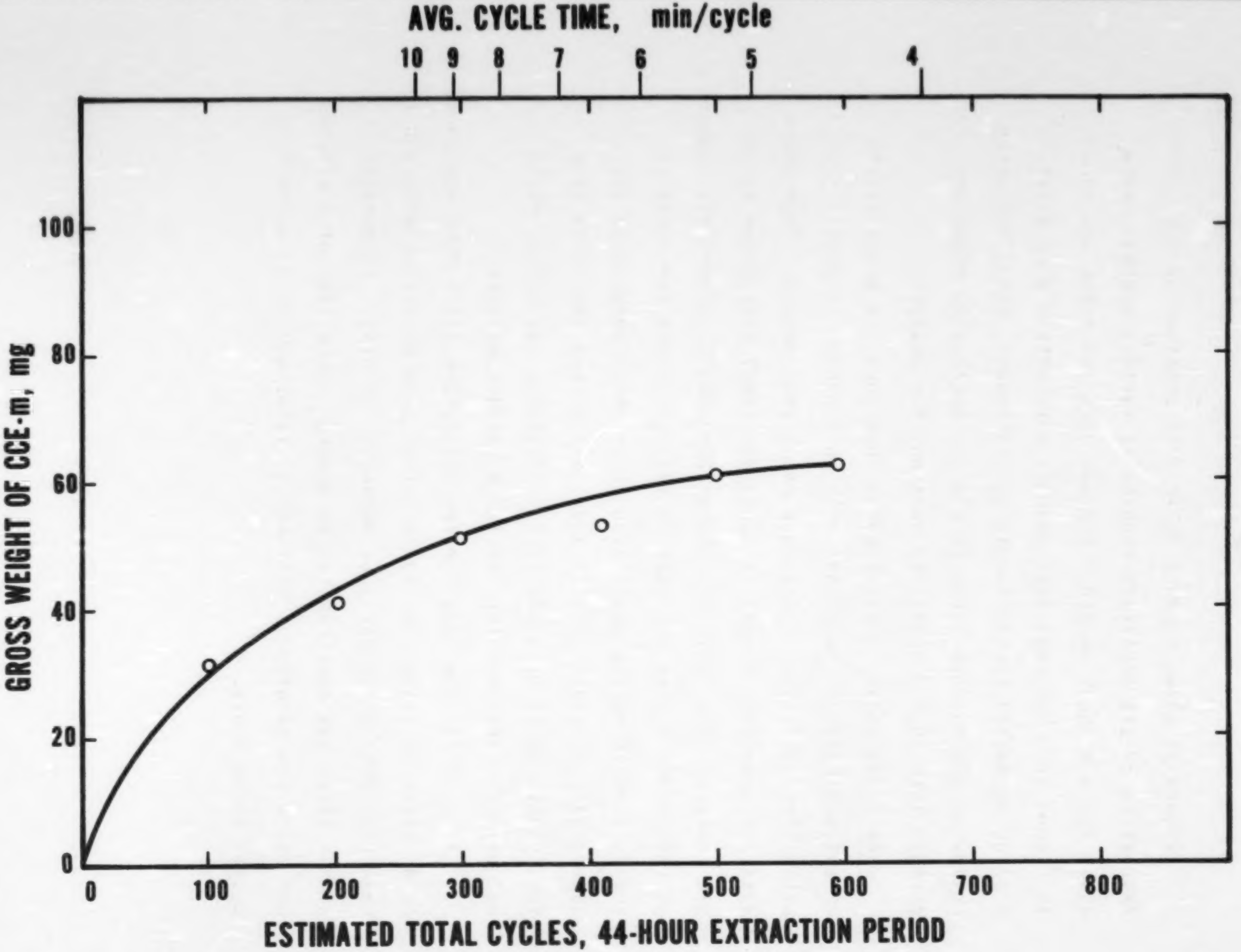


FIGURE 11 - GROSS WEIGHT OF CCE-m VS. TOTAL CYCLES

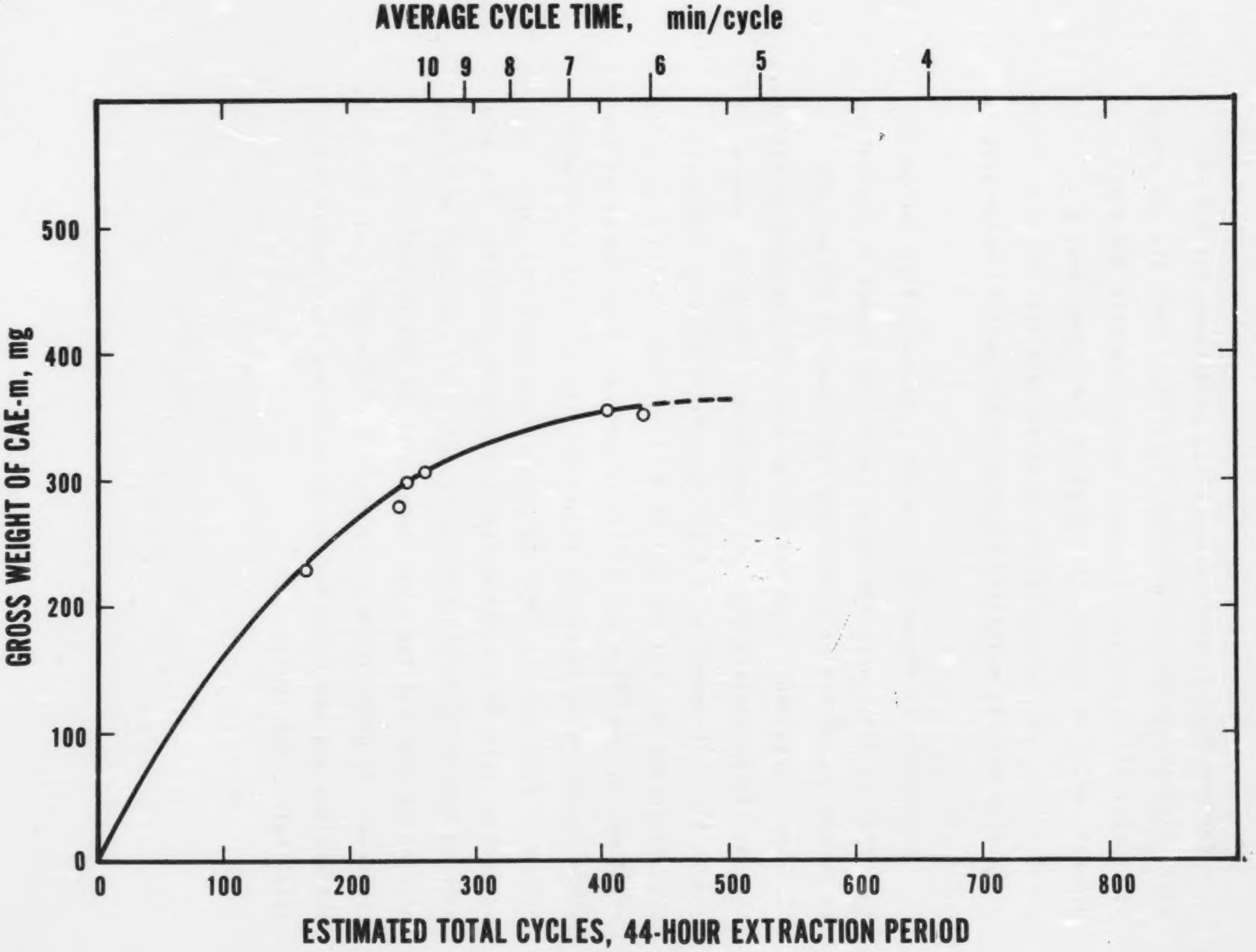


FIGURE 12 - GROSS WEIGHT OF CAE-m VS. TOTAL CYCLES

For simplicity, similar operating conditions for the 95% ethyl alcohol extraction would be desirable. This did not prove to be possible, however. A 6-min. cycle time with 95% ethyl alcohol, with its higher boiling point and higher heat of vaporization, was not consistently attainable with the 6-position extraction heater, primarily because of the heat transfer problem noted above.

Inspection of Figure 12 indicates, however, that for CAE-m an operating limit near 450 total extraction cycles is desirable to reduce the effect of cycle time variations on the weights of extract obtained. Experimentation with equipment modifications, such as higher-wattage heaters, insulation, special glassware, etc. led to the achievement of a 6-1/2 min. cycle time as a practical operating parameter for CAE-m. To meet the total extraction cycle requirement, the CAE-m extraction period was increased to 48 hours. These operating rules result in essentially the same calculated number of total cycles (443) as result from the 6-min/cycle, 44-hour extraction used in the CCE-m test and permits operation from mid-morning Wednesday to mid-morning Friday. The remainder of Friday morning is then available for completion of the analysis and clean-up. By using these procedures, both the CCE-m and the CAE-m extractions are conducted for essentially the same number of total extraction cycles.

Near the end of the method's developmental stage, information was received on a high-temperature, quartz fabric heating mantle. A unit was obtained and, with a variable transformer control, tested as an extraction heater. Operated without modifications, the mantle-heated system easily reached the operating limits established with the modified hot plate-type equipment, and was judged easier to set-up and operate. At these operating limits, the mantle is operating well below its maximum heating capacity, a condition that should extend its service life. For these reasons, the limits were retained, and the use of the mantle recommended in the proposed method (see Appendix).

Variation and Control of Cycle Times

Achieving and maintaining proper solvent cycle times is the key to satisfactory performance of the extraction portion of the O-CA test. During the course of an extraction, keeping cycle times constant would be desirable to reach a certain number of total cycles within a fixed time period. In practice, however, cycle times do vary, sometimes considerably, even when extraction heater settings, a major influence, are kept constant. This variation produces a range of cycle times, the average of which should be within the allowable values specified for the method, 5.5-6.5 m/cycle for chloroform extraction and 6.0-7.0 m/cycle for 95% ethanol extraction. The goal in practice then, is to minimize cycle time variations and produce an acceptable average.

One variable that affects cycle time is ambient temperature. Table 8 illustrates, for one extractor of a multiple set-up, the variations caused in cycle times spot-checked during the course of an extraction that was subjected to widely varying room temperatures. The air temperatures listed in the Table were measured in the immediate vicinity of the extractor and are therefore higher than might be expected for typical room temperature. The temperature variations shown, however, are solely related to room temperature changes, as the extraction heater setting was constant during the period of record. The Table shows, as expected, that cycle times are inversely related to the air temperature in the vicinity of the extractor.

Table 8

INFLUENCE OF AMBIENT TEMPERATURE VARIATIONS ON CYCLE TIME

Date	Time	Extraction Heater Setting	Air temp. in vicinity of the extractor, °C	Cycle Times, min. and sec.
11/17/71	1527	Constant	35.5	6:13
11/18/71	0705	"	36.5	6:08
"	0910	"	35.5	6:22
"	1105	"	34.5	6:28
"	1257	"	35.5	6:23
"	1454	"	36.0	6:21
"	0702	"	37.5	6:07
"	0909	"	37.0	6:14
"	1051	"	35.0	6:21

Although the analyst may not be able to control all ambient temperature variation, he can do several things to lessen its effect: 1) If possible, select a room with the smallest possibledaily temperature variation; 2) Move the extraction equipment to a draft-free location or place it in a hood where the draft is more constant; or 3) If moving the equipment is not possible, shield the extractors (sides and back) from drafts with cardboard.

Extract Drying and Weighing

Drying of extracts obtained from the current (1971) Standard Methods (13) extraction procedures has presented problems to some analysts. The major problem encountered is when to stop the drying and daily weighing of the extract, so that a final result may be recorded. This problem stems from the fact that extracts continue to lose weight, through solvent evaporation and/or extract volatilization, as drying continues. Often, no constant final weight is reached, and thus the analyst has no absolute "end point" to stop his drying and weighing procedure.

Extracts obtained from the O-CA extraction procedure are no exception to the drying problem, as shown in the typical weight loss vs. drying time data presented in Figure Nos. 13 (CCE-m) and 14 (CAE-m). The data shown in these Figures was obtained by drying CCE-m or CAE-m extracts in an unheated mechanical convection oven (temperature approximately 30°C), in which the circulating air was directed into the vial through a tube.

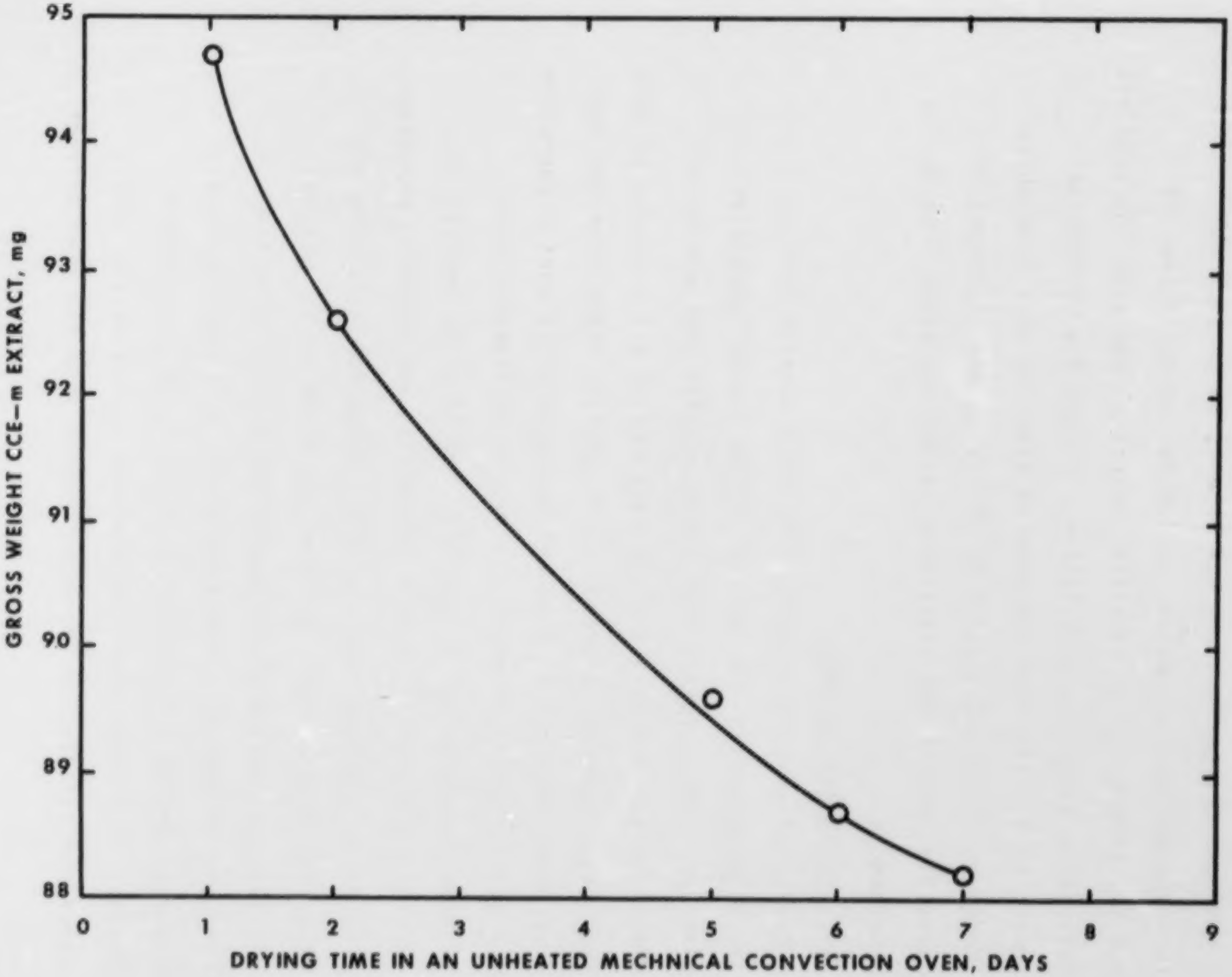


FIGURE 13
WEIGHT OF CCE—m EXTRACT VS. DRYING TIME

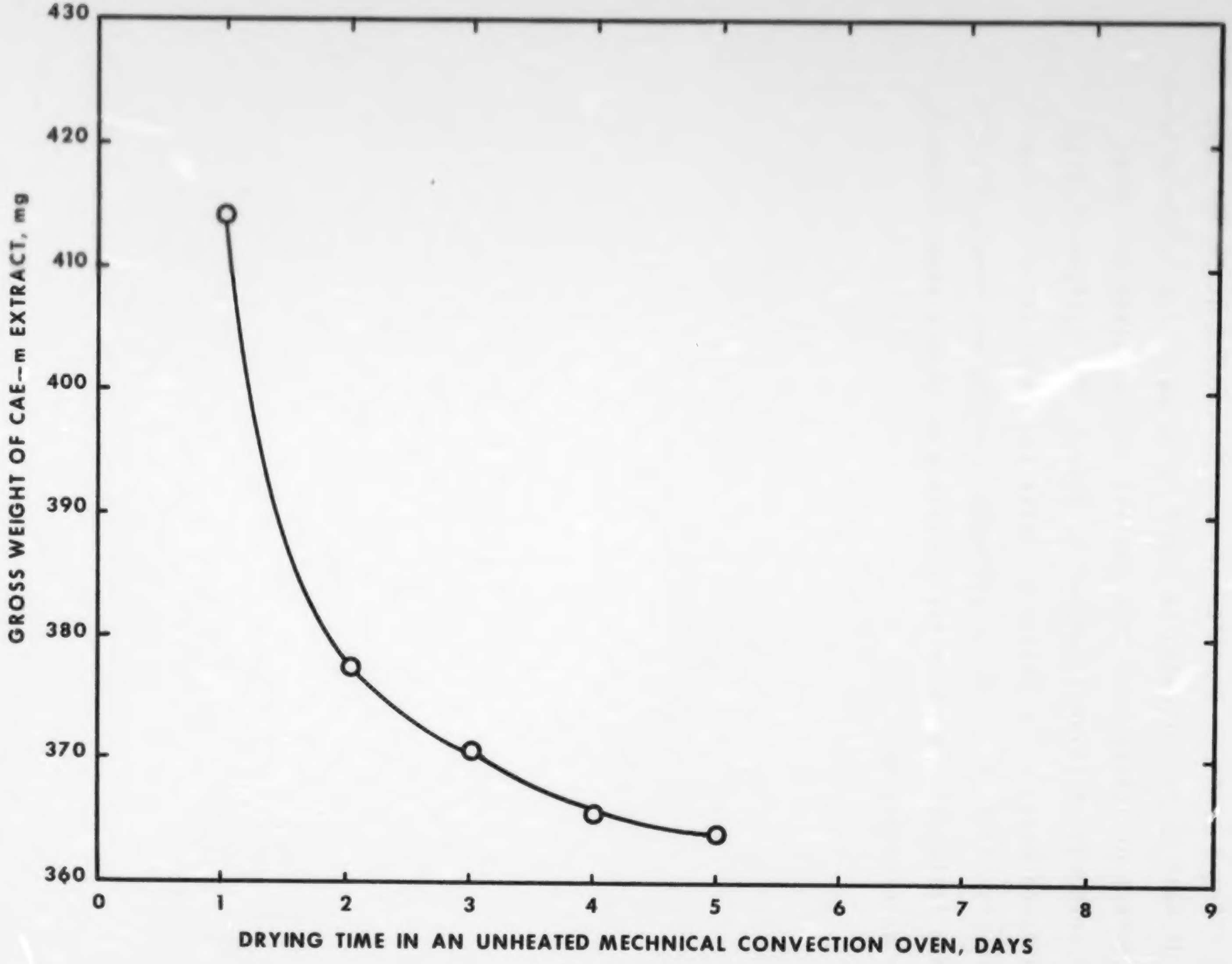


FIGURE 14
WEIGHT OF CAE—m EXTRACT VS. DRYING TIME

In the CCE-hf and CCE-lf procedure in Standard Methods (13) the final extract is transferred to a tared vial and evaporated to dryness by "---allowing to stand in an open hood (without heat) overnight or longer---." The analyst is instructed to "judge completeness of solvent removal by odor." The analyst is also cautioned that "It is better to leave traces of solvent rather than risk loss of sample by prolonged heating and evaporation." These instruction provide the analyst with only a vague endpoint for extract drying.

The CAE-1f procedure of Standard Methods (13) provides the analyst with a more detailed drying and weighing method. After transfer to a tared vial, the CAE-1f extract is initially dried on a steam bath with a jet of air. Drying is continued in a 75°C oven until "--the weight change of successive weighings at 72-hour intervals is less than 1%". This method provides the more vigorous drying needed for the heavy, hard-to-dry CAE-1f extracts, and gives the analyst a better end point by terminating drying and weighing at a fixed weight change percentage. A similar approach was used as the basis for the development of a drying and weighing procedure for this determination.

Experimentation showed that a less vigorous drying procedure could be used on the smaller quantities of extract obtained from the Mini-sampler. Using only a dry, oil-free stream of air directed into the vial with a tube, CCE-m's and CAE-m's from a variety of drinking water samples were found to reach an initial state of dryness within 24 hours. Note: While chloroform will evaporate readily at room temperature, a moving air stream is necessary to hasten the evaporation of 95% ethyl alcohol. Unaided, a 5 dram vial filled with 95% ethyl alcohol required 10 days to evaporate to dryness at room temperature. The photograph, Figure 15, shows a simple device made of wood, 1/8 inch O.D. copper tubing and 6-gang valves that permit the initial drying of six vials at once. A small

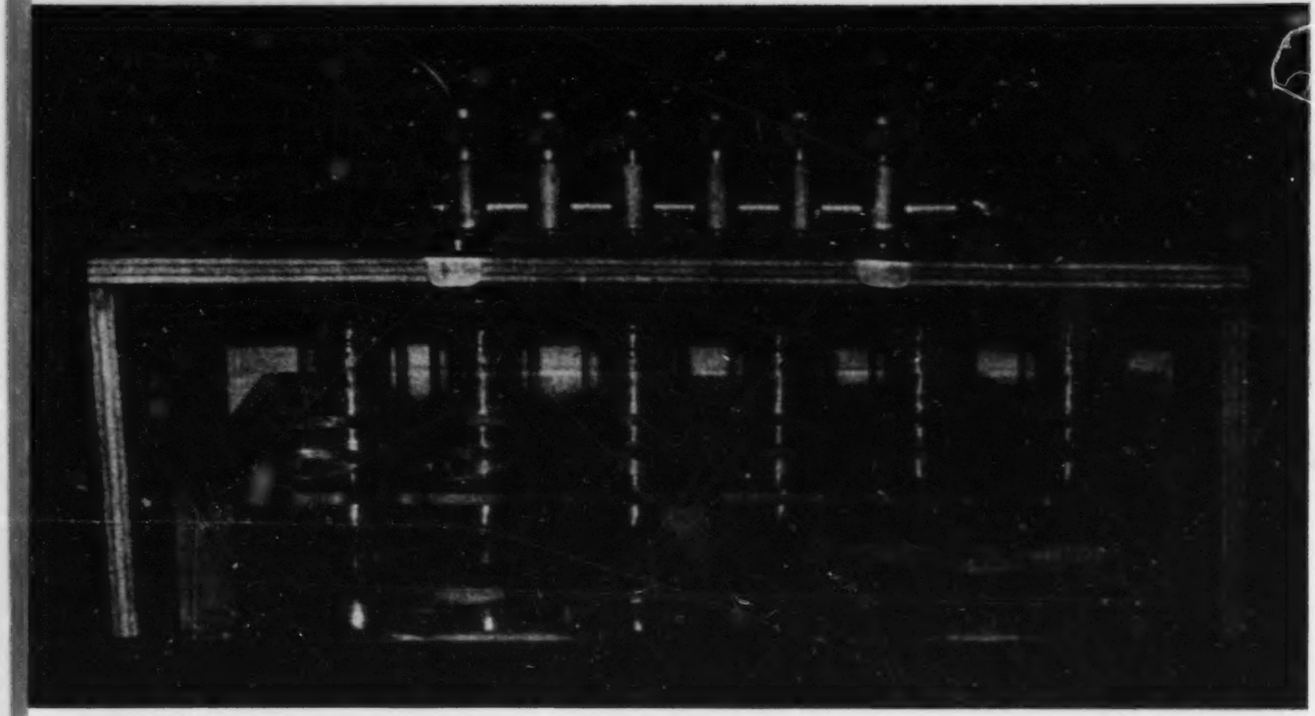


Figure 15. Drying Device for Air Drying Six Vials

cardboard box with a stopper in the top and one face removed, or a similar device would be satisfactory for drying a single sample. Something must cover the vial to prevent debris from accidentally falling in during drying.

As a criterionto determine if the initial state of dryness has been reached after 24 hours, a vial, held with small forceps, is tippedand the contents examined to determine if they will flow to the lower side of the vial. Occasionally, a CAE-m will show evidence of flow after 24 hours under the air stream. In this case, the vial is returned to the air stream to be re-checked after an additional 24 hours of drying.

When flow is no longer evident, the vial is given its initial weighing and then placed in an ordinary laboratory desiccator. The data from the initial weighing is used to calculate the CCE-m and CAE-m concentration in mg/l, rounding the result to the nearest 0.1 mg/l. After 24 hours in the desiccator, the vial is again weighed and the concentration is calculated, rounded, and compared to the initial value. If the concentrations agree, the drying is stopped and the value is reported as the final result. If the concentration has decreased, the desiccator drying and daily re-weighing is continued until the concentrations calculated on two successive days agree. For most extracts obtained from drinking water samples examined to date (1972), this procedure takes two days for CCE-m and three or four days for CAE-m.

Determination of Blank Values

Standard Methods (13) recommends the determination of separate activated carbon and reagent blanks for its high-flow and low-flow CAM extraction methods. For the O-CA method, however, a combined reagent - activated carbon blank is used because of the smaller quantities of activated carbon blank extracts and reagent residues. To determine the combined blank, the O-CA extraction procedure is performed on 70.0 gram replicate samples from a given batch of activated carbon. An average weight of extract obtained from the extraction of a minimum of four replicates is suggested for use as the blank.

Determination of this average combined blank is relatively simple when several extraction set-ups are used. If a single extractor is used, however, the determination of four replicate blanks becomes quite time-consuming. This problem may be avoided by using the special sampling activated carbon, pre-analysed for blank values of CCE-m and CAE-m, available from the Calgon Corporation, Pittsburgh, Pennsylvania.

A special problem arises in the drying and weighing of blank extracts. Because no "volume of water sampled" is associated with a blank, no concentration can be calculated to determine when to stop the drying process using the method noted above. Therefore, an arbitrary endpoint has been defined to provide a uniform procedure for all analysts.

For the CAE-m blank, a procedure patterned after that used for CAE-1f (13) was adopted. By definition, blank CAE-m's are considered dry when the weight change at successive 24-hour intervals is ≤ 1 percent of the former value. Using the standard procedure of air followed by desiccator drying, CAE-m blanks generally reach the weight change limit within three to five days.

The CAE-m blank weight limit definition cannot be applied to CCE-m blanks. Because CCE-m blank values are quite small (≤ 5.0 mg CCE-m/70.0 gm activated carbon), imposition of a weight change limit of 1 percent per day would require drying and weighing to a weight change ≤ 0.05 mg. This value is beyond the limit of readability (0.1 mg) and equals the precision (± 0.05 mg) of a typical 4-place digital read-out macro-analytical balance. For this reason, CCE-m blanks are dried, using the standard procedure, until their weight change at successive 24-hour intervals is = 0.1 mg. Most CCE-m blanks reach this goal in two to three days.

Table 9 presents data from the simultaneous extraction of six replicate blank samples. Table 10 presents data from the extraction of six replicate samples from a different batch of activated carbon. These samples were not extracted simultaneously, but in pairs over a 3-week period.

The data in these Tables illustrates a range of blank values that may be expected from the extraction of the activated carbon used in the O-CA method. Because of only limited experience with two different batches of activated carbon, the significance of the differences in average blank values between batches of activated carbon is unknown at this time (1972). Use of the commercially available sampling activated carbon is recommended to avoid problems with blanks.

Table 9

CCE-m AND CAE-m BLANK VALUES
EXTRACTION RUN OF 9/20/71
ACTIVATED CARBON BATCH NO. 1

Extractor Number	CCE-m Blank, mg	CAE-m Blank, mg
1	2.7	39.3
2	3.8	46.5
3	5.1	42.5
4	3.8	49.2
5	2.8	49.2
6	Extract lost in lab accident	48.7
Average value	3.6	45.9
Standard deviation	1.0	4.1

Table 10

CCE-m AND CAE-m BLANK VALUES
EXTRACTION RUN DATES AS SHOWN
ACTIVATED CARBON BATCH NO. 2

Date of Extraction Run	Extractor Number	CCE-m Blank, mg	CAE-m Blank, mg
11/15/71	1	3.6	44.7
"	6	3.8	57.0
11/22/71	1	1.9	47.8
"	6	1.8	55.2
11/29/71	3	2.1	54.5
"	4	2.0	53.4
Average value		2.5	52.6
Standard deviation		0.9	3.9

Extraction Solvent Reuse

To determine if the extraction solvents recovered as distillates during the solvent volume reduction step in the O-CA method could be reused, a series of gas chromatographic (GC) analyses were conducted. Samples included fresh solvent, recovered distillate, and a composite of recovered distillates diluted with fresh solvent to make up volume losses which occur during extraction and volume reduction.

For chloroform, the GC analyses showed that some impurities are present in the distillate, but in concentrations probably not exceeding 1 percent. As these recovered distillates are composited for reuse, a build-up of impurities is prevented by the large (up to 60 percent) fresh solvent dilution required to offset losses. This was verified by GC examination of the diluted chloroform distillate composite collected during the O-CA method development. The reuse of these chloroform distillates, diluted with fresh chloroform as needed, is recommended.

Analysis of the 95 percent ethyl alcohol distillates showed significant concentrations of impurities, the principal one being residual chloroform. A build-up of these impurities in a distillate composite cannot be offset with the small (40 percent maximum) fresh solvent make-up required for the CAE-m procedure. For this reason, reuse of the 95% ethyl alcohol distillates is not recommended.

Equipment Cost and Size Reduction

As stated before, one of the major objectives in the development of the O-CA method was to make it sufficiently attractive that water treatment plant operators would make the determination part of their regular quality control program. The use of smaller and less expensive extraction equipment that does not require special hoods is a major factor in satisfying this objective.

Cost

Aside from not requiring special hoods for the extraction apparatus the principal item of cost reduction in extraction equipment is the cost of the basic condenser-extractor-boiling flask set-up. Based on 1971 prices, the cost of the large Soxhlet set-up used with the high- and low-flow CAM sampler is approximately \$170. The cost of the small Soxhlet set-up used with the proposed O-CA method is approximately \$45, a cost reduction of almost 75 percent. The cost of a single extraction set-up, glassware, heating mantle, variable transformer, and stand is only about \$110.

The other cost reduction that will result from the use of the smaller extractors is the elimination of the large distillation-type hoods usually used in conjunction with the large Soxhlet units. Because of the reduced solvent volume, the small Soxhlet units can be operated satisfactorily on the bench top in a well-ventilated laboratory. To prevent needless inhalation of solvent vapors, however, the air-stream drying of activated carbon between the CCE-m and CAE-m extractions, the distillation and final volume reduction steps, and the air drying of the extract should be conducted in an ordinary laboratory hood.

Size

Because of the smaller size, the space required for the extraction apparatus is correspondingly reduced. Figure 16 is a photograph of two large extractors in their special distillation hood. Figure 17 is a photograph of the small O-CA extraction set-up as might be used at a water treatment plant.

Typical Extraction Schedule and Time Requirements

The following is a typical 5-day schedule for performance of the CCE-m and CAE-m extractions. The daily man-hour requirements, listed below, are for the operation of a single extractor. Glassware washing, although not included in this weekly schedule, should not add to the overall time requirement as it can be conducted simultaneously with many other operations.

The schedule is flexible and many operations can be performed at any convenient time during the week. The schedule assumes that all extracts will be weighed and dried until they meet the concentration requirement of the method, even if this means occasional additional weighings on the weekend. To minimize weekend work, however, the start of drying of the CAE-m vials is deferred until the following Monday.

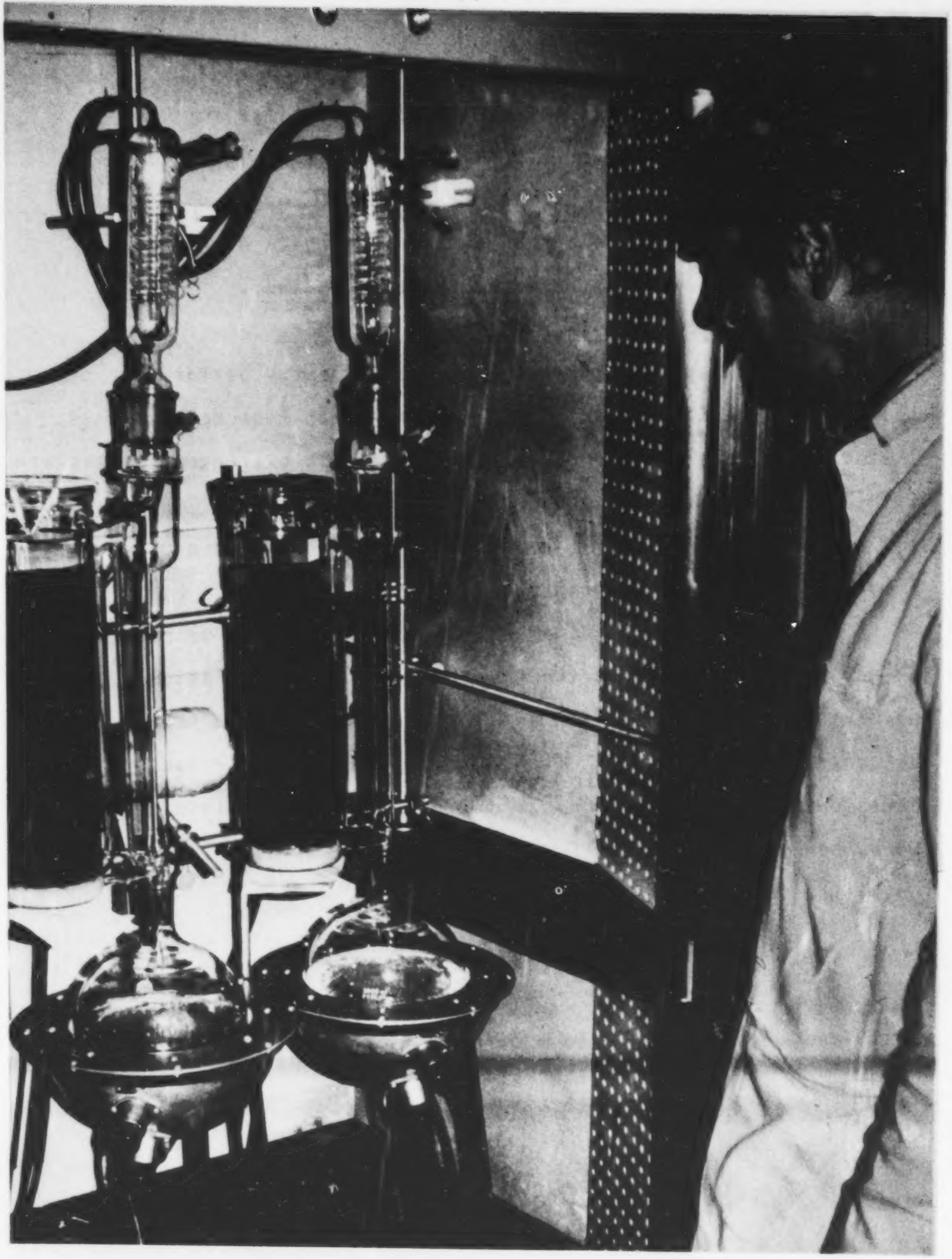


Figure 16. Two Large Extractors for Use with High- or Low Flow CAM Sampler. Note Special Hood Required.

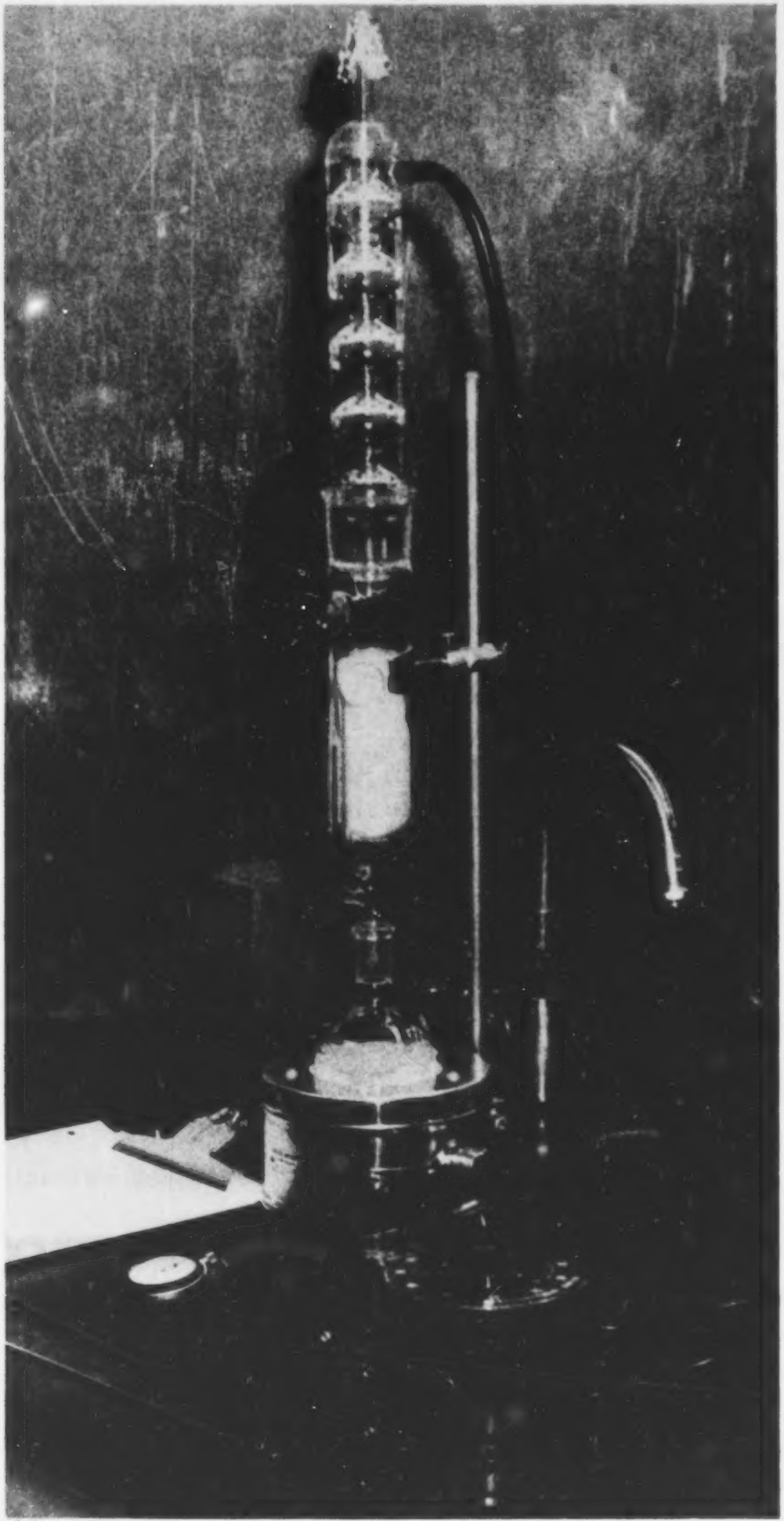


Figure 17. Extractor for Use with Mini-Sampler

Weekly Schedule - Activated Carbon Extractions

(All time requirements are based on the use of a single extraction set-up.)

Monday: 0.8 man-hour

1. Prepare sample and set up equipment for CCE-m extraction.
2. Begin CCE-m extraction at 12 Noon.
3. Begin checking CCE-m cycle times at 1400 hrs.
4. Begin air drying CAE-m vials from last week, if any.
5. Tare this week's vials and return to desiccator.

Tuesday: 0.8 man-hour

1. Continue checking CCE-m cycle times throughout the day, at least 3 times.
2. If dry, weigh last week's CAE-m and place in desiccator.

Wednesday: 1.8 man-hours

1. Stop CCE-m extraction at 0800 hrs. and complete CCE-m procedure.
2. Begin air drying CCE-m vial.
3. Dry thimble and set up equipment for CAE-m extraction.
4. Begin CAE-m extraction at 0930 hrs.
5. Begin checking CAE-m cycle times at 1130 hrs.
6. Continue weighing and drying last week's CAE-m vial as necessary.
7. Calculate average cycle time for CCE-m extraction.

Thursday: 0.8 man-hour

1. Continue checking CAE-m cycle times throughout the day - at least 3 times.
2. If dry, weigh CCE-m vial and place in desiccator.
3. Continue weighing and drying last week's CAE-m vial as necessary.

Friday: 1.8 man-hours

1. Continue checking CAE-m cycle time during the early morning - at least once.
2. Stop CAE-m extraction at 0930 hrs., complete CAE-m procedure and store vial (covered) until next Monday.
3. Continue weighing and drying CCE-m vial as necessary.
4. Number next week's vials and place in desiccator.
5. Calculate average cycle times for CAE-m extraction.

Total: 6.0 man-hours/week

Although the overall time required to obtain final extraction results, usually Monday to Friday for CCE-m and Wednesday to following Thursday for CAE-m has not been significantly shortened when compared to high- and low-flow CAM extractions, the number of man-hours has been reduced. In a water treatment plant processing one sample per week, only about 15 percent of an analyst's time would be required to accomplish the extraction portion of the O-CA determination. In our laboratory, 16 man-hours were required for the routine extraction of six samples/week by the O-CA method.

Reproducibility

While miniaturization of the CAM technique is attractive from several aspects, maintaining good reproducibility in spite of an approximate 10-fold reduction in extract weights was also an objective of this investigation. Reproducibility of the extraction portion of the O-CA method is illustrated for several types of samples in Table No. 11. In this Table, exposed samples are replicates taken from a single large carbon column exposed to

Cincinnati, Ohio tap water, unexposed samples are activated carbon blanks taken directly from the shipping container. These data show reproducibility to be satisfactory. Reproducibility of the overall O-CA method is presented in the Discussion. Two factors that contribute to the good reproducibility are: 1) extraction for a sufficient number of total cycles so that an error of a few cycles during the determination has little influence on the final extract weight (Figures 11 and 12), and 2) having a definite endpoint for terminating extract weighing.

Table No. 11

REPRODUCIBILITY OF THE EXTRACTION PORTION OF THE O-CA METHOD

			CCE-m, uncorrected for blank				CAE-m uncorrected for blank			
Sample	Analyst Number	n	$\bar{X}$, mg	σ,mg	Range mg	RSD %	$\bar{X}$, mg	σ, mg	Range mg	RSD %
Unexposed	1	5	2.2	0.1	0.3	4.5				
Unexposed	1	6(1)	3.6	1.0	2.4	28	45.9	4.1	9.9	8.9
Exposed(3)	1	6	87.0	1.7	4.7	2.0				
Exposed	1	6	86.6	2.8	7.3	3.2	344.3	6.4	19.4	1.8
Exposed	2	6	66.3	5.2	12.8	7.8	263.7	27.7	82.6	10.5(2)
Exposed	2	4	63.8	2.0	4.6	3.1	257.5	11.2	23.7	4.3

Notes: (1) n = 5 for CCE-m; 1 extract lost in lab accident.

(2) May have been influenced by contaminated solvent.

(3) Extracts weighed daily during drying until Δweight/day $\leq$ 1% of previous day's weight.

DISCUSSION

General Improvements

The development work reported in this paper has resulted in a technique for the determination of the general organic concentration in water by adsorption on activated carbon and desorption with two organic solvents, called Organics - Carbon Adsorbable (O-CA); a method that is relatively inexpensive, simpler than previous similar determinations, reliable and does not require many man-hours to perform. It is adaptable for use in most water treatment plant laboratories as well as in large central laboratories. A color, sound, 16 mm movie entitled "The Determination of Organics in Drinking Water" showing how the O-CA test is performed may be borrowed from the Director, Water Supply Research Laboratory, National Environmental Research Center, 4676 Columbia Parkway, Cincinnati, Ohio 45268. Running time is about 50 minutes.

Although the final results from the O-CA test are not available for several days after sampling begins, this is not a serious flaw in the method, because it is intended for general monitoring and not as a technique for detecting a sudden influx of organic pollution. A "once-a-week" monitoring schedule might start sampling on Wednesday morning, start adsorbant drying on Friday morning, and start extraction on the following Monday at noon. A "continuous" monitoring schedule would collect the first sample from Monday morning through Wednesday morning; the exposed activated carbon being dried for 24 hours and stored until extraction begins. The second sampling of the week would start Wednesday morning and end Friday morning, the exposed activated carbon also being dried for 24 hours and stored until extraction begins. The third sample would be collected from Friday morning to Sunday morning. The third adsorbant sample is dried until Monday morning and all three samples of activated carbon are extracted starting Monday noon. Using this schedule, monitoring would be continuous, except for Sundays.

Reproducibility

One objective of this study was to maintain good reproducibility while miniaturizing the method. Published data on the reproducibility of the High- and Low-Flow CAMs for comparison is extremely limited. The current (1971) edition of Standard Methods (13) mentions only that for CAE-hf's, "Replicate samples agree within ± 10%". The Low-Flow Method contains no mention of reproducibility or agreement among replicates.

In 1965, Booth, English, and McDermott (9) reported the results of an investigation of the reproducibility of the Low-Flow CAM. Their data were obtained from the analysis of four low-flow activated carbon columns operated in parallel on Ohio River water. A portion of their data is presented in Table 12.

Table 12

REPRODUCIBILITY OF THE LOW-FLOW CAM TECHNIQUE

[Data from Booth, English and McDermott (9)]

	CCE-1f	CAE-1f
n	4	4
$\bar{X}$	0.261 mg/l	0.259 mg/l
σ	0.004 mg/l	0.001 mg/l
Range	0.004 mg/l	0.025 mg/l
RSD	1.6%	4.1%

Two tests were conducted to determine whether reducing the sample volume from the usual 1200 liters of the Low-Flow CAM technique resulted in a significant change in reproducibility. In these two tests replicate Mini-Samplers were exposed to Cincinnati, Ohio tap water at a sample flow rate of 20 ml/min. The first set of four sampled about 200 liters of water while the second set sampled about 100 liters. Table 13 shows that good reproduciblity is possible with the O-CA test. These concentrations were calculated to three decimals as has been done in the past (13) and then analyzed statistically. The magnitude of the standard deviation indicates that concentration data should only be reported to the nearest 0.1 mg/l.

Table 13

REPRODUCIBILITY OF THE O-CA DETERMINATION

(Sampling by Analyst Number 3)

Test 1

(Extraction by Analyst Number 1)

	CCE-m	CAE-m
1	0.314 mg/1	0.932 mg/1
2	0.332 mg/1	1.068 mg/1
3	0.338 mg/1	1.020 mg/1
4	0.334 mg/1	1.109 mg/1
n	4	4
$\bar{X}$	0.330 mg/1	1.032 mg/1
σ	0.010 mg/1	0.076 mg/1
Range	0.024 mg/1	0.177 mg/1
RSD	3.0%	7.4%

Test 2

(Extraction by Analyst Number 2)

1	0.485 mg/1	1.494 mg/1*
2	0.493 mg/1	1.789 mg/1
3	0.522 mg/1	1.888 mg/1
4	0.507 mg/1	1.780 mg/1
5	0.499 mg/1	1.872 mg/1
6	0.511 mg/1	1.963 mg/1
n	6	6
$\bar{X}$	0.503 mg/1	1.799 mg/1
σ	0.013 mg/1	0.163 mg/1
Range	0.037 mg/1	0.469 mg/1
RSD	2.6%	9.1%

*One of the six replicates produced a surprisingly low concentration. The remaining 5 samples had an $\bar{X}$ = 1.860, σ= 0.073, Range = 0.183 mg/1 and RSD= 3.9%. The authors think this is a better representation of the reproducibility of the determination than the data presented.

Field Data

Increased Yield

To determine the increased yield of the O-CA method over the Low-Flow CAM technique, parallel determinations were made on finished water at three different locations for a total of 27 weeks. Table 15 shows a nearly three-fold increase in yield, although the CCE-m/CCE-1f ratio data has a fairly high relative standard deviation.

Table 15

ORGANIC YIELD OF O-CA COMPARED TO LOW-FLOW CAM

(Data from Three Locations)

	CCE-m/CCE-1f	CAE-m/CAE-1f
n	29	29
$\bar{X}$	2.9	3.0
σ	1.1	0.5
Range	4.0	1.8
RSD	37%	18%

For the water supply industry the increase in yield of this method from the High Flow Method, upon which the 1962 U.S. Public Health Service Drinking Water Standards (1962 DWS) were based, is of interest. Although no parallel studies were made comparing these two methods, an estimate of the yield increase can be obtained by combining the data in Tables 1 and 15. By multiplying the average yield ratios in these two tables together (see Eq. 1) an approximation of the increased yield of the O-CA method over the high flow CAM results.

$$\frac{\text{CCE-lf}}{\text{CCE-hf}} \times \frac{\text{CCE-m}}{\text{CCE-lf}} = \frac{\text{CCE-m}}{\text{CCE-hf}} \qquad \text{Eq. 1}$$

Note: The CAE yield ratios may be multiplied together in the same manner.

The reason this is only an estimate is because each average yield ratio in Table 1 and 15 has a fairly high relative standard deviation. Combining the data in Tables 1 and 15 shows that the CCE-m/CCE-hf ratio is 6.7/1 and the CAE-m/CAE-hf ratio is 20.4/1, although the latter cannot be related to the 1962 DWS because it was not included in those standards.

CCE-m and CAE-m Concentrations

Once the O-CA method was developed and standardized (See Appendix), CCE-m and CAE-m concentrations were determined in a variety of locations and on a variety of types of waters. The purpose of collecting these data was to gain some experience with the concentration of CCE-m and CAE-m to be expected under actual operating conditions.

These data, summarized in Table 16, show that this technique can determine extract concentrations within about a ten-fold range between clean water and surface waters heavily influenced by upstream waste discharges.

Table 16

ORGANICS - CARBON ADSORBABLE DETERMINATION ON VARIOUS WATERS

				CCE-m			CAE-m		
Location	Source	Description of Water	Season	n	Avg. mg/l	Min.-Max. mg/l	n	Avg. mg/l	Min.-Max. mg/l
Ohio	Well	Finished, after softening	Winter	2	0.1	0.1-0.1	2	0.4	0.3-0.4
Ohio	Spring	Stored in small open reservoir	Autumn	3	0.1	0.1-0.2	3	0.6	0.6-0.6
Michigan	Lake St. Clair	Settled	Autumn	10	0.3	0.2-0.4	10	1.2	0.8-1.6
Michigan	Lake St. Clair	Settled	Winter	3	0.3	0.3-0.3	2	1.5	1.5-1.5
Ohio	Great Miami River	Finished, Act. Carbon beds exhausted	Summer	9	0.4	0.3-0.4	9	1.7	1.6-1.9
Ohio	"	"	Autumn	2	0.6	0.5-0.6	2	1.6	1.1-2.1
Ohio	Ohio River	Tap	Autumn	13	0.4	0.3-0.5	13	1.2	0.9-1.5
"	"	"	Winter	8	0.5	0.4-0.5	8	1.8	1.4-2.0
Massachusetts	Merrimack River	Finished, Act. carbon beds exhausted	Summer	5	0.8	0.8-0.9	5	2.8	2.3-3.5
"	"	"	Autumn	4	0.9	0.7-1.0	5	2.5	2.2-2.6
"	"	Settled	Winter	9	1.2	0.8-3.1	9	5.0	4.0-7.4
West Virginia	Kanawha River	Settled	Spring	3	0.5	0.5-0.5	2	4.5	4.1-4.9

Table 16 (Contd.)

Location	Source	Description of Water	Season	CCE-m			CAE-m		
				n	Avg. mg/l	Min.-Max. mg/l	n	Avg. mg/l	Min.-Max. mg/l
Pennsylvania	Schuylkill River	Finished	Winter	1	0.7	-	1	2.3	-
	Delaware River	Finished	Winter	1	0.5	-	1	1.2	-
Maryland	Liberty Reservoir	Finished	Winter	1	0.4	-	1	1.2	-
	Loch Raven Reservoir	Finished	Winter	1	0.4	-	1	2.6	-
District of Columbia	Potomac River	Finished	Winter	1	0.3	-	1	1.5	-
Pennsylvania	Allegheny River	Finished	Winter	1	0.3	-	1	1.9	-
New Jersey	Oradell Reservoir	Finished	Spring	1	0.7	-	1	2.0	-
Minnesota	Lake Superior	Raw	Summer	2	0.2	0.2-0.2	2	0.8	0.7-0.8

CONCLUSIONS

Based on the results of this study, the following conclusions are drawn:

1) The Mini-Sampler is a reliable, convenient method of concentrating organics on activated carbon.

2) The companion extraction procedure is a convenient method of desorbing organics from activated carbon with organic solvents.

3) The cost of the Organics - Carbon Adsorbable (O-CA) determination has been significantly reduced over that of previous CAM methods.

4) Field testing of the O-CA method (to be proposed as a "standard method") showed it to be simpler than previous similar methods and to be satisfactory, both for raw, settled, or finished water. It should be able to be performed in most water plant laboratories.

5) Comparison to the High-Flow CAM technique showed about a seven-fold increase in yield in CCE and about a twenty-fold increase in CAE.

6) Sampling a variety of waters showed clean ground water to have a CCE-m concentration of about 0.1 mg/l and a CAE-m concentration of about 0.3-0.4 mg/l. Surface waters heavily influenced by upstream discharges of wastes show about a ten-fold increase over these concentrations.

ACKNOWLEDGMENTS

The authors wish to thank the following persons who contributed to the completion of this project and the preparation of the paper and method.

Mr. William R. Snider and Mr. Reynold A. Hardenbrook, who collected the Great Miami River samples.

Mr. William McCarthy who collected the Merrimack River samples.

Mr. Robert Hansen and Mr. Gerry Charbonneau who collected the Lake St. Clair, Michigan samples.

Dr. Gary S. Logsdon and Mr. Jesse Royer who collected the well water samples.

Mr. Edward Dean who collected the Kanawha River samples.

Mr. James Manwaring, Mr. Edwin Lippy and Mr. Frank Hertsch who in cooperation with the respective water plant personnel collected the Schuylkill, Delaware, Potomac, and Allegheny River and the Liberty and Loch Raven Reservoir samples.

Mr. Michael Dworsky who collected the Oradell Reservoir samples.

Mr. Richard McKee, Calgon Corporation, Pittsburgh, Pennsylvania who helped evaluate and modify the method.

Mr. Frank Reis and Dee Cole for their help in early construction of the Mini-Sampler when materials and equipment were in short supply.

Mr. Robert Mills and Mr. Vernon Maxson who supplied the high-flow CAM and low-flow CAM data.

Mr. Donald E. Mitchell who helped install many of the Mini-Samplers and performed many of the extractions.

Mr. Douglas Kuehl who collected the Lake Superior samples.

Mrs. Maura M. Lilly who patiently typed and retyped many drafts of this paper and the associated operational manual.

Mr. Robert Booth, Mr. Jesse Cohen, Mr. Earl F. McFarren, Dr. Aaron Rosen, Mr. Leland J. McCabe and Mr. Gordon G. Robeck for reviewing the method and/or this paper.

GLOSSARY

CAM: Carbon adsorption method for determining the general organic content of water. It involves adsorption of organics on activated carbon and desorption with organic solvents.

CCE-hf: Carbon-chloroform extract obtained by chloroform extraction of an activated carbon sample from a High-Flow (0.25 gpm - 945 ml/min) CAM sampler.

CCE-lf: Carbon-chloroform extract obtained by chloroform extraction of an activated carbon sample from a Low-Flow (120 ml/min) CAM sampler.

CCE-m: Carbon-chloroform extract obtained by chloroform extraction of an activated carbon sample from a Mini-Sampler.

CAE-hf: Carbon-alcohol extract obtained by 95% ethyl alcohol extraction (preceded by chloroform extraction) of an activated carbon sample from a High-Flow (0.25 gpm) CAM sampler.

CAE-lf: Carbon-alcohol extract obtained by 95% ethyl alcohol extraction (preceded by chloroform extraction) of an activated carbon sample from a Low-Flow (120 ml/min) CAM sampler.

CAE-m; Carbon-alcohol extract obtained by 95% ethyl alcohol extraction (preceded by chloroform extraction) of an activated carbon sample from a Mini-Sampler.

Cycle Time: The elapsed time in minutes and seconds, measured with a stopwatch, between the start of two consecutive siphon cycles in the Soxhlet extractor.

Mini-Sampler: A miniaturized and simplified CAM sampler.

n: The number of samples or observations in a set of data.

O-CA: Organics-Carbon Adsorbable - contains two parts, Carbon-Chloroform Extract (CCE-m) and Carbon Alcohol Extract (CAE-m) both of which have an operational definition.

RSD: Relative standard deviation of a set of data, calculated by the equation, $RSD = \sigma/\bar{x} \times 100$, expressed as a percent.

Range: The difference between the maximum value and the minimum value in a set of data.

σ(Sigma): The standard deviation of a set of data calculated by the equation

$$\sigma = \sqrt{\frac{\Sigma(x-\bar{x})^2}{n-1}}$$

If the set of data is normally distributed, 95 percent of the data will be between $\bar{x} + 2\sigma$ and $\bar{x} - 2\sigma$.

Total Cycles: An estimate of the total number of siphon cycles an activated carbon sample undergoes during the extraction period. The estimate is calculated by:

(1) spot checking cycle times throughout the extraction period.

(2) calculating an arithmetic average cycle time.

(3) dividing the time of extraction by the average cycle time to yield an estimate of the total number of cycles.

$\bar{X}$: Arithmetic average or mean of a set of data, calculated by the equation $\Sigma(x_1 + x_2 + \ldots + x_n)/n$.

REFERENCES

1. Braus, H., Middleton, F.M., and Walton, G., "Organic Chemical Compounds in Raw and Filtered Surface Waters," _Analytical Chemistry_, 23, 8, 1160-1164 (Aug. 1951).
2. Middleton, F.M., Braus, H., and Ruchhoft, C.C., "Fundamental Studies of Taste and Odor in Water Supplies," _JAWWA_, _44_, 6 538-546 (June 1952).
3. Middleton, F.M., Braus, H., and Ruchhoft, C.C., "The Application of the Carbon Filter and Countercurrent Extraction to the Analysis of Organic Industrial Wastes," Proceedings of the Seventh Industrial Waste Conference, Engineering Bulletin, XXXVI, 6, 439-454, Purdue University, Lafayette, Indiana (Nov. 1952).
4. "Tentative Method for Carbon Chloroform Extract (CCE) in Water," _JAWWA_, _54_, 2, 223-227 (Feb. o962).
5. Taylor, F.B., Smith, H.F., Jr. and Coene, R.F., "Alternative Sampling Device for the Carbon Adsorption Method," _JAWWA_, _56_, 774-780 (June 1964).
6. Ettinger, M.B., "Proposed Toxicity Screening Procedure for Use in Protecting Drinking-Water Quality," _JAWWA_, _52_, 6, 689-694, (June 1960).
7. Heuper, W.C. and Payne, W.W., "Carcinogenic Effects of Adsorbants of Raw and Finished Water Supplies," _The American Journal of Clinical Pathology_, _39_, 5, 475-481 (May 1963).
8. _Federal Register_, _27_, 2152-2155 (March 6, 1962).
9. Booth, R.L., English, J.N. and McDermott, G.N., "Evaluation of Sampling Conditions in the Carbon Adsorption Method," _JAWWA_, _57_, 215-220 (Feb. 1965).

10. Castelli, J.A. and Booth, R.L., "Low-Flow Liquid Meter," JAWWA, 56, 1243-44 (Sept. 1964).

11. Reid, B.H., Stierli, H., Henke, C. and Breidenbach, A.W. "Field Evaluation of Low-Flow-Rate Carbon Adsorption Equipment and Methods for Organics Sampling of Surface Waters," PHS Water Pollution Surveillance System Applications and Development Report #14, Division of Water Supply and Pollution Control, U.S. Department of Health, Education and Welfare (currently Robert A. Taft Water Research Division, National Environmental Research Center, U.S. Environmental Protection Agency, Cincinnati, Ohio (March 1965) Mimeo, 31 pp.

12. Installation, Operation and Maintenance of Models No. LF-1 and LF-2, Organics Samplers for Water, Division of Pollution Surveillance, Federal Water Pollution Control Administration, U.S. Department of the Interior (currently Robert A. Taft Water Research Division, National Environmental Research Center, U.S. Environmental Protection Agency) Cincinnati, Ohio (Revised Dec. 1967) 12 pp.

13. Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, American Public Health Association, New York, New York (1971) 874 pp.

14. McCabe, L.J., "Life Table Analysis of Heuper's Data," Interoffice Memo, Jan. 23, 1964, Robert A. Taft Sanitary Engineering Center (currently) U.S. Environmental Protection Agency, Cincinnati, Ohio 45268 (Unpublished).

15. Rosen, A.A., Middleton, F.M., and Taylor, N.W., "Identification of Anionic Synthetic Detergents in Foams and Surface Waters," JAWWA, 48, 1321-1330 (Oct. 1956).

16. Allen, S.C., Pahl, R.H. and Mayhan, K.G., "Organic Desorption from Carbon-I. A Critical Look at Desorption of Unknown Organic Materials from Carbon " Water Research, 5, 1, 3-18 (Jan. 1971).

17. Robeck, G.G. and Dostal, K.A., "Progress Report on Activated Carbon Experiments," Interoffice Memo, March 26, 1962, Robert A. Taft Sanitary Engineering Center (currently) U.S. Environmental Protection Agency, Cincinnati, Ohio 45268 (Unpublished).

APPENDIX
PROPOSED METHOD FOR
ORGANICS - CARBON ADSORBABLE

Organic contaminants - natural substances, insecticides, herbicides, and other agricultural chemicals - enter water supplies from precipitation runoff. Domestic sewage and industrial wastes, depending upon the degree of treatment, contribute contaminants in various amounts. As a result of accidental spills and leaks, industrial organic wastes also enter streams. Some of the contaminants, extremely persistent and only partially removed by treatment, reach the consumer in drinking water.

Contaminants, both natural and man-made, can conceivably have undesirable effects on health (1)(2). Some of these materials interfere with water quality by causing tastes and odors and killing fish. The isolation and recovery of insecticides, nitriles, ortho-nitrochlorobenzene, aromatic ethers, waste hydrocarbons, and many other synthetic chemicals suggest that a method for assessing these materials in water is desirable.

Organics - Carbon Adsorbable (O-CA), as used here, contains two parts, Carbon-Chloroform Extract and Carbon-Alcohol Extract, both of which have an operational definition. CCE-m is a mixture of organic compounds that can be adsorbed on activated carbon under prescribed conditions and then desorbed with the solvent chloroform. CAE-m is a mixture of organic compounds that can be adsorbed on activated carbon and then desorbed with the solvent 95 percent ethyl alcohol after the chloroform soluble organics have been desorbed under prescribed conditions (3). The lower case letter "m" is used to denote that these parameters are determined by using a miniaturized sampler and extraction technique and to distinguish it from the high-flow (hf) and low-flow (lf) carbon adsorption method (CAM) technique recommended in the 13th Edition of Standard Methods. (4). The O-CA method is a modification of this earlier work (5)(6)(7).

1. General Discussion

a. Principle

This is a gravimetric adsorption/extraction method. Organic materials adsorbed on a sample of activated carbon are removed by sequential extraction with two organic solvents. The extracts are processed by volume reduction through distillation and drying. The quantities of organic materials are then determined gravimetricall

b. Inadequacies

Some organic compounds may not be adsorbed on activated carbon or recovered from the activated carbon by the solvents used in this method causing a negative error. Inorganic substances may contribute to the weight of extract obtained causing a positive error.

c. Application

This method is useful for sampling water that contains organic matter mostly in the dissolved form. Examples of this type of water are drinking water, surface water, and ground water. Because the adsorption capacity of the activated carbon is limited, this technique would not work well on waters containing high concentrations of organics, such as wastes. .

This method is primarily for monitoring the general organic content of water and is not designed as a collector of organics for further identification, although, with certain precautions, the resulting extracts can be reprocessed. Although all adsorption-desorption techniques have inherent limitations, this method does not require expensive instrumentation, divides the organics into two general classes, chloroform soluble and alcohol soluble, and should be within the capabilities of most water treatment plant laboratories as well as central laboratories. While the toxicological studies on the components of CCE-m and CAE-m are not complete at this time (1972), control of the concentrations of CCE-m and CAE-m in drinking water will protect the consumer as these studies continue.

The proposed 1972 U.S. Environmental Protection Agency Drinking Water Standards state that the concentrations of CCE-m and CAE-m in drinking water shall not exceed 0.7 mg/l and 3.0 mg/l respectively, to protect the consumer against unwarranted levels of organic matter.

Typical values of these two parameters are shown below:

CLASS OF SAMPLE	mg/l CCE-m	mg/l CAE-m	
Well Water	0.1	0.4	(Avg. of 2)
Spring Water Stored in Small Pond	0.1	0.6	(Avg. of 3)
Finished Water from Lightly Polluted Surface Water, Autumn	0.3*	1.2*	(Avg. of 10)
Finished Water from Moderately Polluted Surface Water - A, Summer	0.4*	1.7*	(Avg. of 11)
Finished Water from Moderately Polluted Surface Water - B, Winter	0.5*	1.9*	(Avg. of 5)
Finished Water from Heavily Polluted Surface Water, Summer & Autumn	0.9*	2.7*	(Avg. of 9)
Winter	1.2	4.5	(Avg. of 9)

*These concentrations are about three times CCE-1f data on the same water (3).

d. Sampling and Storage

In addition to the normal precautions to obtain a representative sample, a special sampler described in Section 4 must be used. Because the throughput volume for this sampler is about 60 liters, direct preservation of a water sample is inconvenient. If necessary, however, the dried, exposed activated carbon sample can be stored in sealed glass containers at about 4°C.

e. Appendix Material

The Appendix contains information of interest to all analysts, but is not part of the actual procedure. Sections that have explanatory information in the Appendix are designated with a check mark and a number "(✓-No.)", the number referring to the section of the Appendix. Analysts are urged to review this material.

2. Apparatus

a. Boiling flask, 300 ml, round or flat bottom, borosilicate glass, ₮ 24/40 joint (2 required)

b. Condenser, Graham, outer ₮ 24/40 joint

c. Distilling column packing, berl saddles, porcelain, 6 mm

d. Drying tray, stainless steel, 8-7/8" long, 5" wide and 2" deep. Do not use aluminum or galvanized metals for trays because they react with wet activated carbon.[1]

e. Extraction apparatus, Soxhlet, with Allihn condenser, borosilicate glass, 50 mm I.D. extractor, ₮ 55/50 top joint, ₮ 24/40 bottom joint.

f. Extraction thimbles, paper, seamless, fat free, single thickness, 43 mm I.D., 123 mm length.

g. Filtering screen, 40-mesh, stainless steel

h. Forceps, aquarium, metal[2]

i. Forceps, small, metal, to handle berl saddles and vials.

j. Heating mantle, Glas-Col No. STM-800, for extraction step (✓-1)

k. Heating mantle, Glas-Col No. M-104, for distillation step (✓-1)

l. Mechanical convection oven, that can be regulated to a temperature of 40° ± 1° C.[3] (✓-1)

m. Miniature CAM Sampler[4] (See Figure 1 and Reference 8)

n. Miniature CAM Sample Columns (See Figure 2 and Reference 8)

o. Stopper, polyethylene, hollow, ₮ 24/40 cone size

p. Stopwatch

q. Transformer, variable output, 10 amp., 120 V.

r. Tube, connecting, distilling, borosilicate glass, ₸ 24/40 joints.

s. Tubing, Latex, black, 1/4 in. I.D. by 1/16 in. wall

t. Vials, 5 dram, flint glass, with polyethylene stopper

---

1 - Matheson Scientific No. 63127-10, Trays - Instrument, Stainless Steel, Round Corners, 1 qt. capacity has been found satisfactory for this purpose.

2 - Turtox No. 205A40 has been found satisfactory for this purpose. Any forceps with a large tip surface area to avoid tearing the thimbles is satisfactory.

3 - The Blue M, Model OV-490 A-C has been found satisfactory for this purpose.

4 - These samplers have been built for the U.S. Environmental Protection Agency by Sea World Research and Development Laboratories, P.O. Box 308, North Wilbraham, MA 01067.

3. Reagents

a. Activated carbon, granular, coal base, 14x40 mesh grain size, Filtrasorb 200[5]

b. Chloroform, Reagent A.C.S., (✓-2)

c. Compressed air, dry, oil-free[6]

d. Ethyl Alcohol, U.S.P., 95 percent[7] (✓-2)
(Do not use absolute or denatured alcohol).

---

[5] - Filtrasorb 200, manufactured by the Calgon Corporation, Pittsburgh, Pennsylvania has been found satisfactory as the adsorbant. They manufacture a special sampling activated carbon with the CCE-m and CAE-m blank values per 70.0 gm of activated carbon predetermined.

[6] - If a central source of compressed air is not available, a small air pump such as Fisher Scientific Co. No. 1-092-5, Dyna-Pump or a small tank of compressed air should be satisfactory.

[7] - Footnote 7 on top of page [redacted]. 90

FIGURE 1

SCHEMATIC OF MINIATURE CAM SAMPLER (MODEL A) (MODEL B DOES NOT HAVE PARTS M-P AND REPLACES THEM WITH A CALIBRATED COLLECTION VESSEL)

A - Constant Head Main Tank
B - Sample Column Feed Tank Valve
C - Sample Column Feed Tank
D - Flushing Valve
E - Sample Column
F - Flushing Solenoid Valve
G - Sample Column Flow Regulating Valve
H - 30-Minute Timer
I - Delay Timer - Set for 7-8 Seconds
J - Power ON-OFF switch
K - Duplex Outlet
L - Sample Column Outlet Tube
M - Volume Measuring Tank
N - Volume Measuring Solenoid Valve
O - Volume Measurement Control
P - Digital Counter Volume Recorder

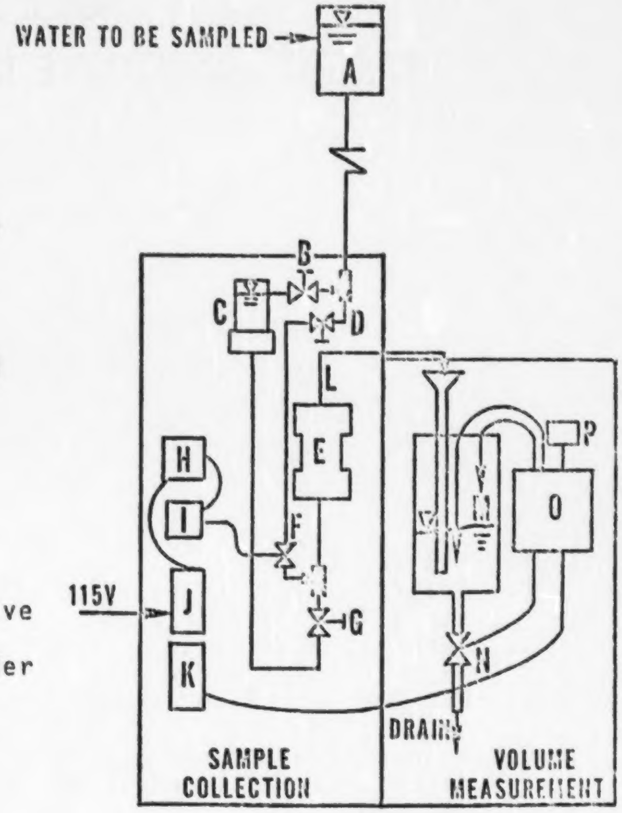
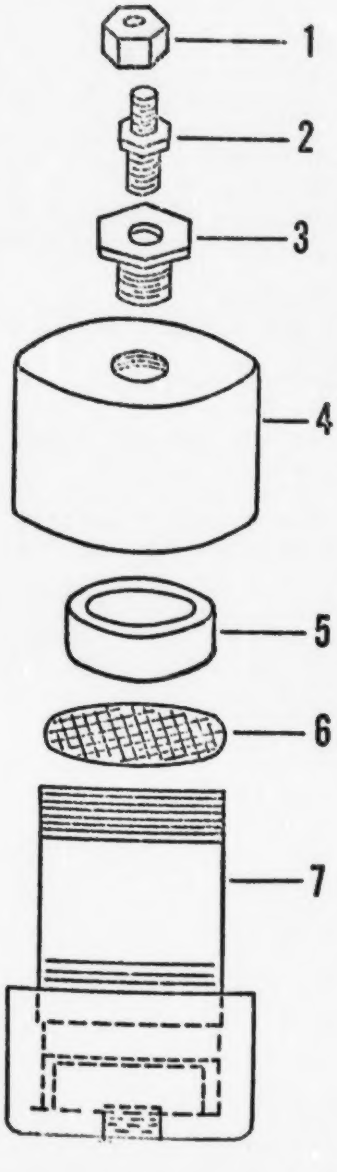

WATER TO BE SAMPLED
A
B
C
D
L
E
H
I
F
J
G
K
115V
M
P
O
N
DRAIN
SAMPLE COLLECTION
VOLUME MEASUREMENT

FIGURE 2

MINIATURE CAM SAMPLE COLUMN ASSEMBLY



1. Fitting Cap
2. Adapter - 1/4 in. pipe to 1/4 in. O.D. tubing
3. Bushing, pipe, brass, 1/2 in.x 1/4 in.
4. PVC End Cap, Pipe Thread PVC Schedule 80
5. Spacer screen support, 1-1/2 in. PVC Schedule 80 5/8 in. high
6. Screen, 2-1/4 in. dia. Stainless steel wire cloth 40x40 mesh, wire dia. 0.012 in.
7. Nipple, pipe, PVC Schedule 80, 2 in. pipe threaded, 3 in. long

Note: Both ends are identical.

7 - Ethyl Alcohol, U.S.P., 95%, may be purchased as follows:

1. Taxed ethyl alcohol may be purchased in 1-gallon lots or in cases of 24 pints from various suppliers, including the U.S. Industrial Chemicals Company, a Division of National Distillers and Chemical Corporation. The current (1972) price from this source is approximately $26 per gallon of which approximately $20 is Federal tax.

2. Purchase of tax-free ethyl alcbhol requires a permit issued by the Alcohol, Tobacco and Firearms Division of the U.S. Treasury Department. Purchasers desiring to obtain permits should contact the Assistant Regional Commissioner, AT&F Division, of the Federal region in which they are located for further information.

4. Procedure

A brief description of the Miniature CAM sampler operation will precede the portion of this section that deals with the collection of the sample.

A parts list and construction drawings and a manual on the installation, operation, and maintenance of the Miniaturized CAM Sampler (8) are all available from the Director, Water Supply Research Laboratory, National Environmental Research Center, U.S. Environmental Protection Agency, 4676 Columbia Parkway, Cincinnati, Ohio 45268.

The miniature CAM sampler apparatus schematic drawing is shown in Figure 1. The sampler operates with a low constant head of water (less than 3 ft.). The water to be sampled is supplied by gravity from a very low constant head tank (less than 5 in.) and flows upward through 70.0 g of activated carbon at a rate of about 20 ml/min (4.5 minute contact time) for a 48-hour period, thereby sampling about 60 liters of water. Once each 30 minutes the activated carbon is flushed automatically for 7-8 seconds (in the same direction as sample flow) at a flow rate of about

400 ml/min. This increased upward flow rate (flushing) expands the carbon in the column slightly and washes out air and fine particles that would impede flow.

The sampler can be operated on high or low pressure water supplies and requires 115 volt electrical power to operate the flushing cycle timers, the solenoid valves and the volume measuring apparatus if Model A is used. Note: If sufficient water pressure is not available or cannot be created by use of a siphon, a small pump must be employed. This pump must be constructed of materials that will not introduce organics into the water or allow lubricants to contaminate the sample.

a. Preparation of Sample Column - Figure 2

Place 70.0 g of activated carbon in the miniature CAM sample column. Apply a double layer of Teflon tape on the column threads for first time use and a single layer for repeat uses. When teflon tape builds up on the threads so that it interferes with assembling the column, it must be completely stripped off and taped as for first time use. Using this procedure the column can be assembled so as not to leak by hard hand tightening of the PVC end cap. This also allows for disassembly by hand. Tools such as a vice and strap wrench may be used. Note: Experience will show users the degree of tightness necessary to prevent leaking. Care in wrapping of the Teflon tape on the threads is the best leak preventive measure. Excessive tightening is unnecessary and should be avoided because it shortens the effective length of the sample column, thereby reducing the space for the 70.0 gm of activated carbon and restricting the cleansing of the activated carbon during flushing

b. Start of Sampling

Attach sample column to column inlet connection, clamp column to board and connect sample column outlet tube. Turn power switch on and open sample column flow regulating valve fully until a stream of water flows from the sample column outlet tube. This should take less than one minute. Close sample column regulating valve, then reopen 2-1/2 turns. Measure sampling flow in graduated cylinder and adjust to about 20 ml/min.

If not previously set, open flushing valve about 3/4 turns. Activate flushing timer and check flushing volume - 50-55 ml during the 7-8 second flushing. Adjust flushing valve as necessary. Note: If desired, the 30-minute timer can be set so that one flush occurs at any fixed minute during an hour. This way the time during any hour to check flushing can be known.

Recheck sampling flow with graduated cylinder about 1-2 hours after start-up. Readjust if necessary.

c. Daily During Sampling (2 Days)

Once the flushing volume has been set, a daily visual check of the flushing flow should be satisfactory. A decrease in flushing volume can result in column blocking. Check the sample flow rate once a day. If it is outside the range 18 ml/min - 22 ml/min, adjust flow rate to about 20 ml/min with the column flow regulating valve. Usually the sample flow rate does not require adjustment during the sampling period.

Record the volume counter reading and the date and time of reading on sample form if Model A is used. If Model B is used, expected daily levels can be marked on the collection container and checked. About 31 liters should pass through the sampler each 24 hours.

d. End of Sampling

Shut off sample column flow regulating valve and power switch. Record final volume counter reading - Model A - or final volume in collection container - Model B. Remove sample column outlet tubing from top of column. Remove column clamp and tilt column forward slightly.

Place fitting cap on top fitting of column. Loosen sample column inlet connection and remove column. Drain water from column by removing fitting cap from top fitting. Place fitting caps on fittings at both ends of column, finger tight.

If the screen in the main tank is being coated by floc or particulates it should be cleaned. If main tank or sample column feed tank show a build-up of sediment, they should be cleaned by brushing and flushing. The sampler can be stored between runs full of water with the sample column flow regulating valve and power switch off.

e. Emptying Sample Column

Remove activated carbon sample from the column as soon after collection as possible. Loosen one of the PVC end caps by hand or tools depending on tightness of cap. Remove fitting caps to permit air to enter the sample column during activated carbon removal.

Remove loosened PVC end cap while holding column over and close to the drying tray. Remove the bulk of the activated carbon from the column and PVC end cap by tapping together and catching the activated carbon in the drying tray, being careful to prevent spilling of activated carbon outside of the tray. The activated carbon still adhering to the column surfaces is rinsed directly into the drying tray by a stream of distilled water from a squeeze bottle. Note: The few granules of activated carbon remaining in the column after thorough rinsing are not enough to alter the final results. Care should be taken, however, to keep activated carbon loss to a minimum in this and subsequent steps.

Shake the drying tray lightly to distribute the activated carbon evenly in the tray. The activated carbon layer will be about 3/16" in depth. Without shifting the carbon distribution, remove excess water by slowly pouring from a corner of the tray. This excess water is drained through a screening device [8] that will retain any activated carbon particles that flow off with the water. Particles retained by the screening device should be returned to the tray.

f. Drying of Activated Carbon

Place drying tray containing wet activated carbon sample in a mechanical convection drying oven regulated to a temperature of 40 ± 1°C. Dry at 40 ± 1°C for at least 24, but not more than 72 hours. (✓-3) Note: The drying oven must be located in a dust and organic vapor free area. Paint fumes or other organic vapors will be adsorbed by the activated carbon and cause false result

---

[8] - A 40-mesh circular stainless steel screen pressed into an 80 mm polypropylene powder funnel has been found satisfactory for this purpose.

g. Storage of Dried Activated Carbon Samples

If extraction is delayed, the dried activated carbon samples should be stored at about 4°C in clean pint glass containers with screw-on lids.

h. Extraction (See Appendix for typical schedule)

Add 250 ml of chloroform to the 300 ml boiling flask. Add 10 berl saddles (rinsed in chloroform) as boiling stones. Stopper the flask to prevent solvent evaporation and place in the Glas-Col STM-800 heating mantle. Place a sample of dried activated carbon in the extraction thimble. Place the thimble in the Soxhlet extractor with the aquarium forceps, place the extractor on the boiling flask, and add the condenser.

Extract the sample for 44 hours, adjusting the transformer to attain an initial extraction cycle time of 6 min ± 15 sec per cycle. As a minimum, cycle times should be checked after about 2 hours of operation and three or four times during the second day of extraction. Readjust the transformer setting if times are less than 5.5 min per cycle or more than 6.5 min per cycle. (✓ -3)

Some loss of solvent through the glass joints and condenser will occur during the course of the extraction. Periodically observe the level of the solvent remaining in the boiling flask when the extractor is ready to siphon. This solvent level should never be allowed to fall below the aluminum top surface of the mantle. Special attention should be given to this problem if the extractor will run unattended overnight. Additions to the solvent volume can be made by slowly pouring small quantities (approx. 25 ml of fresh solvent down the top opening of the condenser.

Turn off the heating mantle and allow the apparatus to cool 15 minutes before removing the condenser. Transfer the extraction solvent remaining in the extractor to the 300 ml flask by draining and removing the thimble with the aquarium forceps, and tipping the extractor-flask assembly to start the siphon. Remove the flask from the heating mantle. Drain additional solvent from the thimble into a beaker and add drainage to the 300 ml flask. Stopper the flask to prevent evaporation.

While Step "i" is being completed on the CCE-m, the thimble and activated carbon are air-dried in the extractor. Move the extractor into a hood to prevent discharge of solvent fumes into the laboratory. Gently blow dry, oil-free air into the extractor for at least 1 hour or until ready to begin the CAE-m extraction, through a latex rubber tube attached (lightly) to the effluent end of the siphon tube. Flexible vinyl tubing should not be used, as it has been found difficult to remove from the siphon tube without breakage.

Perform the CAE-m by repeating Steps "h" and "i" noting the following procedure changes:

1) Extraction solvent is 95 percent ethyl alcohol.

2) Extraction time is 48 hours.

3) Initial extraction cycle time is 6.5 min. ± 15 sec per cycle. Readjust the transformer setting if cycle times are less than 6.0 min per cycle or more than 7.0 min per cycle.

i. Reduction of Solvent Volume

Before beginning the solvent volume reduction step, inspect the contents of the 300 ml flask for carbon particles. If any are evident, remove them by filtration through Whatman No. 1 (or equivalent) filter paper. In a hood, using the Glas-Col M-104 heating mantle, connecting tube and Graham condenser, distill off excess extraction solvent until the volume remaining in the 300 ml boiling flask is less than 20 ml. (✓-3). Use transformer settings of about 60 for chloroform and about 75 for ethyl alcohol. Note: The transformer from Step "h" can be used. Occasionally swirl the contents during distillation to dissolve extract from the sidewall. Important: To avoid abrupt, massive boil-over of flask contents, which will terminate the determination, continuous, vigorous swirling of the contents of the 300 ml boiling flask until boiling is well established is necessary. This usually takes 3-5 minutes.

If collection of the solvent is not desired, the excess may be boiled off in a hood without condensing, although the time to reach the desired final volume may be longer (See Appendix, Section 2 for information on solvent reuse).

Remove the 300 ml boiling flask from the still while hot, using a towel or gloves. Swirl contents vigorously to dissolve extract from the sidewall and allow to cool.

Transfer the contents of the 300 ml boiling flask to a clean, tared 5 dram (18 ml) vial, using care to avoid tipping the berl saddles into the vial. Use 2 ml of additional extraction solvent to rinse the flask and berl saddles and add to the vial.

Re-rinse with 1 ml of additional extraction solvent and add to the vial.

j. Drying of Extract

Evaporate the contents of the tared vial to dryness using a gentle stream of dry, oil-free air directed into the vial with a tube. (√-3). After about 24 hours of drying, tilt the vial, using small forceps, to determine if the contents will still "flow." If "flow" is evident, continue drying and re-examine at 24-hour intervals. If extra drying is required, it is usually required with CAE-m extracts.

If "flow" is not evident, weigh vial and calculate the CCE-m or CAE-m concentration. Place vial in a desiccator for 24 hours, reweigh, and recalculate the concentration. If it is unchanged from the previous day, stop drying and report the value as the final result. If the concentration has decreased, continue the desiccator drying and daily reweighing until the concentration is unchanged on two successive days. Do not place CCE-m and CAE-m vials together in the same desiccator. Note: If a delay in the start of extract drying is desirable, a vial may be covered with aluminum foil and stored at room temperature for two or three days without problems.

If the extracts are to be reprocessed for identification of components, some extract from blank activated carbon should also be tested to assure that any compound that is identified did not come from the activated carbon, the solvent, or the thimble, and preclean the vials with detergent wash.

k. Instructions for Cleaning Apparatus

In many of the 300 ml flasks used in the extraction procedure, a scale-like deposit forms on the bottom inner surface. This deposit is usually more extensive in flasks used for CAE-m. To remove the deposit, a thorough brushing with household cleanser and a minimum of water is effective. After brushing, a 24-hour (minimum) soak in chromic acid, followed by a detergent wash with tap and distilled water rinses, is recommended.

5. Computation

$$\text{CCE-m or CAE=m, mg/l} = \frac{[(A-B) \times 1000] - C}{D}$$

Where: A = g weight of vial plus extract

B = g tare weight of vial

C = mg weight of CCE-m or CAE-m average blank (J-4)

D = liter volume of water sampled

Express result to nearest 0.1 mg/l.

Note: Batches of the special sampling carbon, pre-analyzed for blank values of CCE-m and CAE-m are available from the Calgon Corporation, Pittsburgh, Pennsylvania.

6. Precision and Accuracy

While insufficient data is currently (1972) available to calculate precision, some information on reproducibility is available. These data are shown below.

Type of Extract	Analyst Number	Number of Replicates,n	Mean Weight of Extract/ 70.0 gm of Adsorbant, $\bar{X}$, mg	Standard Deviation σ, mg	Coefficient Variation σ/Mean,V, %
UNEXPOSED ACTIVATED CARBON (FROM SHIPPING CONTAINER)					
CCE-m	1	5	2.2§	0.1	4.5
CCE-m	1	5	3.6 §	1.0	28
CAE-m	1	6	45.9**	4.1	8.9
ACTIVATED CARBON EXPOSED IN LARGE CONTAINER, DRIED, MIXED, AND DIVIDED INTO 70.0 gm PORTIONS					
CCE-m	1	6	87.0**	1.7	2.0
CCE-m	1	6	86.6**	2.8	3.2
CCE-m	2	6	66.3**	5.2	7.8
CCE-m	2	4	63.8**	2.0	3.1
CAE-m	1	6	344.3**	6.4	1.8
CAE-m	2	6	263.7**	27.7	10.5*
CAE-m	2	4	257.5**	11.7	4.5

---

*May have been influenced by contaminanted solvent.

**Extract weighed daily until Δweight/day ≦1% previous days weight.

§Extract weighed daily until Δweight/day ≦0.1 mg.

70.0 gm of ACTIVATED CARBON EXPOSED TO SAME WATER IN SEPARATE MINI-SAMPLERS (COLLECTED BY ANALYST NUMBER 3)

Type of Extract	Analyst Number	Number of Replicates,n	Mean Concentration $\bar{X}$, mg/l	Standard Deviation, σ,mg/l	Coefficient c Variation,V-%
CCE-m	1	4	0.330*	0.010	3.0
CCE-m	2	6	0.503*	0.013	2.6
CAE-m	1	4	1.032*	0.076	7.4
CAE-m	2	6**	1.799*	0.163	9.1

---

*Extracts weighed daily until dry to constant concentration, see Procedure Step "j".

**One of the six replicates produced a surprisingly low concentration, 1.494 mg/l. The remaining 5 replicates had an $\bar{X}$ of 1.860 mg/l, a σ of 0.073 mg/l and a V of 3.9%.

The concentrations were calculated to three decimals as has been the practice in the past and then analyzed statistically. Because of the magnitude of the standard deviation, the final extract concentrations should be expressed to the nearest 0.1 mg/l.

Although percentage recovery determinations with known compounds has not been performed at this time (1972), the increase in extract yield (3) over that obtained by previous methods (4) indicates improved accuracy.

7. References

(1) Heuper, W.C. and Payne, W.W.,"Carcinogenic Effects of Raw and Finished Water Supplies," The American Journal of Clinical Pathology, 39, 5, 475-481 (May 1963).

(2) McCabe, L.J., "Life Table Analysis of Heuper's Data," Interoffice Memo, Jan. 23, 1964, Robert A. Taft Sanitary Engineering Center, (Currently) U.S. Environmental Protection Agency, Cincinnati, Ohio 45268. Unpublished.

(3) Buelow, R. W., Carswell, J. K. and Symons, J. M., "An Improved Methods for Determining Organics in Water by Activated Carbon Adsorption and Solvent Extraction," *Journal American Water Works Association*, *64*, (1972)[In Preparati

(4) *Standard Methods for the Examination of Water and Wastewater*, Thirteenth Edition, American Public Health Association, New York, New York (1971) 874 pp.

(5) Booth, R.L., English, J.N., and McDermott, G.N., "Evaluation of Sampling Conditions in the Carbon Adsorption Methods," *JAWWA*, *57*, 215-220 (Feb. 1965).

(6) Reid, B.H., Stierli, H., Henke, C. and Breidenbach, A.W.,' "Field Evaluation of Low-Flow-Rate Carbon Adsorption Equipment and Methods for Organics Sampling of Surface Waters," PHS Water Pollution Surveillance System Applications and Development Report #14, Division of Water Supply and Pollution Control, U.S. Department of Health, Education and Welfare (Currently Analytical Quality Control Laboratory, National Environmental Research Center, U.S. Environmental Protection Agency),Cincinnati, OH (March 1965) Mimeo, 31 pp.

(7) Installation, Operation, and Maintenance of Models Nos. LF-1 and LF-2, Organics Samplers for Water, Division of Pollution Surveillance, Federal Water Pollution Control Administration, U.S. Department of the Interior (Currently Analytical Quality Control Laboratory, National Environmental Research Center, U. S. Environmental Protection Agency,) Cincinnati, OH (Revised Dec. 1967), 12 pp.

(8) Carswell, J.K., Buelow, R. W., and Symons, J.M., "The Determination of Organics - Carbon Adsorbable In Water," Water Supply Research Laboratory, National Environmental Research Center, U. S. Environmental Protection Agency, Cincinnati, Ohio (July 1972), Mimeo, 58 pp.

APPENDIX

1) The following supplementary information applies to items noted in Section 2, Apparatus.

Item j. When purchasing this item, specify if it is to be used for 300 ml round- or flat-bottom flasks according to the choice made for Item a. Do not use flat-bottom flasks in mantles designed for round-bottom flasks.

Item k. See note for Item j, above.

Item l. If a gravity convection incubator operating at 35°C ± 0.5°C as used for incubation of total coliform tubes or plates is available it can be used for activated carbon drying. A test as described in the Appendix, Part 2, Step "f" below should be made, however, to determine the minimum acceptable drying time for the activated carbon. Excess residual moisture will interfere with the subsequent extraction.

2) The following supplementary information applies to the items noted in Section 3, Reagents.

Item b. Chloroform distillate from Procedure, Step "i" may be reused if desired. Gas chromatograhic analysis of this distillate shows that some impurities are present, but in concentrations not exceeding 1 percent. However, a build-up of impurities to significant concentrations in the reused chloroform is prevented by the dilution with unused chloroform required to offset solvent volume losses of up to 60 percent that can occur in the CCE-m procedure. Prevention of this build-up by dilution has been confirmed by GC analysis of a reused-unused chloroform composite.

Item d. Ethyl alcohol distillate from Procedure, Step "i" should not be reused, as GC analysis shows it contains significant concentrations of impurities, the principal one being residual chloroform. Because solvent volume losses in the CAE-m procedure seldom exceed 40 percent, a further build-up in the already significant impurity concentrations in the reused ethyl alcohol will not be prevented by the small make-up volume required.

3) The following supplementary information applies to the steps noted in Section 4, Procedure.

Step f. Studies have shown that in mechanical drying ovens operating at 40°C ± 1°C, at least 24 hours must be allowed to satisfactorily dry the activated carbon. Further tests have shown that drying up to 72 hours at this temperature will not result in a measurable reduction in extract weight. If a mechanical convection drying oven is not available, a gravity convection drying oven or incubator may be used. Checking the drying capabilities of these alternative drying devices is advisable to determine required drying times. This can be done by weighing out 70.0 grams of unexposed activated carbon and soaking in distilled water in a covered glass container for at least 24 hours. Place sample in a tared drying tray, drain excess water, place the sample in the drying device and weigh at 24-hour intervals until the weight of the dried activated carbon (total wt. of Pan + Activated Carbon = Tray tare wt.) is equal to or less than 70.0 grams. The time required to reach this weight will be the minimum drying time allowable for the particular drying device.

Step h. A suggested 5-day extraction schedule is:

1. Monday
   a. begin drying last week's CAE-m
   b. set up extraction apparatus and begin CCE-m extraction at 1200 hours
   c. begin checking CCE-m cycle times
2. Tuesday
   a. weigh and continue drying last week's CAE-m
   b. continue checking CCE-m cycle times
3. Wednesday
   a. Stop CCE-m extraction at 0800 hours and complete CCE-m procedure
   b. begin drying CCE-m
   c. dry thimble and prepare for CAE-m extraction
   d. start CAE-m extraction at 0930 hours
   e. weigh and continue drying last week's CAE-m, if required
4. Thursday
   a. continue checking CAE-m cycle times
   b. weigh and continue drying CCE-m as indicated
   c. weigh and continue drying last week's CAE-m, if required
5. Friday
   a. continue checking CAE-m cycle times
   b. stop CAE-m extraction at 0930 hours and complete CAE-m procedure

c. cover CAE-m vial with aluminum foil and allow to stand until Monday to begin drying

d. weigh and continue drying CCE-m, if required

e. weigh and continue drying CAE-m, if required

Step h. (continued) The weight of extract obtained is directly influenced by the total number of extraction cycles to which the activated carbon sample is subjected. To insure that a total number of cycles within the desired range is obtained, cycle times are spot-checked throughout the extraction, and an average cycle time is computed. An average cycle time in the range called for will produce the 405 to 480 total cycles desired in 44 hours for CCE-m or the 410 to 480 total cycles desired in 48 hours for CAE-m. The proper cycle times should be easily obtainable. Continuous monitoring of the air temperature in the immediate vicinity of the extraction equipment is a useful check on the regularity of operation.

Step i. Some experience is required to determine when to stop the distillation. The volume remaining in the 300 ml boiling flask may be estimated by comparing the original volume to that distilled over into a graduated beaker.

Step j. Vials may also be dried in an unheated mechanical convection oven. The interior of the oven should be modified to direct the air flow into the vials through tubes. If vials are dried in an oven, do not dry anything else with the extracts as their weights may be influenced.

4) The following supplementary information applies to the item noted in Section 5, Computation.

CCE-m blanks are dried, using the standard procedure of air followed by desiccator drying, until their weight change at successive 24-hour intervals is 0.1 mg.

CAE-m blanks are dried, using the standard procedure of air followed by desiccator drying, until their weight change at successive 24-hour intervals is $\leq$ 1 percent of the former value.

☆ U.S. GOVERNMENT PRINTING OFFICE: 1972— 759-548/1018